Text-Books of Physical Chemistry

EDITED BY

SIR WILLIAM RAMSAY K.C.B., F.R.S.

AND

F. G. DONNAN, C.B.E., M.A., PH.D., F.I.C., F.R.S.

TO THE READER

KINDLY use this book very carefully. If the book is disfigured or marked or written on while in your possession the book will have to be replaced by a new copy or paid for. In case the book be a volume of set of which single volumes are not available the price of the whole set will be realized.

AMARSINGH COLLEGE

Library

Class No. 535.84

Book No. B 195. V.2

Acc. No. 5175

ext-2004

TEXTBOOKS OF PHYSICAL CHEMISTRY

EDITED BY SIR WILLIAM RAMSAY, K.C.B., D.Sc., F.R.S.

AND

F. G. DONNAN, C.B.E., M.A., D.Sc., PH.D., F.I.C., F.R.S.

SPECTROSCOPY

TEXTBOOKS OF PHYSICAL CHEMISTRY.

Edited by Sir WILLIAM RAMSAY, K.C.B., D.Sc., F.R.S.,

AND

F. G. DONNAN, C.B.E., M.A., D.Sc., Ph.D., F.I.C., F.R.S.

STOICHIOMETRY. By SYDNEY YOUNG, D.Sc., F.R.S., Professor of Chemistry in the University of Dublin. With 93 Figures in the Text. 8vo. 12s. 6d. net.

THE PHASE RULE AND ITS APPLICATIONS. By ALEXANDER FINDLAY, M.A., Ph.D., D.Sc., F.I.C., Professor of Chemistry at the University of Aberdeen. With 158 Figures in the Text. Crown 8vo. 10s. 6d. net.

SPECTROSCOPY. By E. C. C. BALY, C.B.E., F.I.C., M.Sc., F.R.S., Grant Professor of Inorganic Chemistry in the University of Liverpool, Fellow of University College, London. With Illustrations. Third Edition. In Four Volumes. 8vo. Vol. I., 14s. net.

THERMOCHEMISTRY. By JULIUS THOMSEN, Emeritus Professor of Chemistry in the University of Copenhagen. Translated by KATHARINE A. BURKE, B.Sc. (Lond.). Crown 8vo. 12s. 6d. net.

STEREOCHEMISTRY. By ALFRED W. STEWART, D.Sc., Professor of Chemistry in the Queen's University of Belfast. With 58 Illustrations. 8vo. 12s. 6d. net.

ELECTRO-CHEMISTRY. Part I. General Theory. By R. A. LEHFELDT, D.Sc. Including a Chapter on the Relation of Chemical Constitution to Conductivity. By T. S. MOORE, B.A., B.Sc., Lecturer in the University of Birmingham. With 55 Figures. Crown 8vo. 7s. 6d. net.

METALLOGRAPHY. By CECIL H. DESCH, D.Sc., Ph.D., F.R.S., Professor of Metallurgy in the University of Sheffield. With 14 Plates and 105 Diagrams. Crown 8vo. 16s. net.

A SYSTEM OF PHYSICAL CHEMISTRY. By WILLIAM C. MCC. LEWIS, M.A. (R.U.I.), D.Sc. (Liv.) F.Inst.P., F.R.S., Brunner Professor of Physical Chemistry in the University of Liverpool. 3 vols. 8vo.

Vol. I. Kinetic Theory. With 55 Diagrams. 15s. net.

Vol. II. Thermodynamics. With 55 Diagrams. 15s. net.

Vol. III. Quantum Theory. With certain Appendices by JAMES RICE, M.A., A. M'KEOWN, M.Sc., and R. O. GRIFFITH, M.Sc. With 12 Diagrams. 15s. net.

THE THEORY OF ALLOTROPY. By A. SMITS, Ph.D., Professor of Chemistry in the University of Amsterdam. Translated by J. SMEATH THOMAS, D.Sc., University of Cape Town. With 239 Illustrations. 8vo. 21s. net.

LONGMANS, GREEN AND CO. LTD.,

LONDON, NEW YORK, TORONTO, BOMBAY, CALCUTTA AND MADRAS.

Com-05
Alw-57

SPECTROSCOPY

BY

E. C. C. BALY, C.B.E., M.Sc., F.R.S.

GRANT PROFESSOR OF INORGANIC CHEMISTRY IN THE UNIVERSITY OF LIVERPOOL
FELLOW OF UNIVERSITY COLLEGE, LONDON

THIRD EDITION

IN FOUR VOLUMES

VOL. II

WITH NINETY-FIVE ILLUSTRATIONS
AND THREE PLATES

LONGMANS, GREEN AND CO. LTD.
39 PATERNOSTER ROW, LONDON, E.C. 4
NEW YORK, TORONTO
BOMBAY, CALCUTTA AND MADRAS
1927

2 Vols: 2nd Edn

535.84
B19S
A.S. College
acc 5175

First Edition . . . . . *June*, 1905
Second Edition . . . . . *May*, 1912
New Impression . . *September*, 1918
Third Edition (*four volumes*):
Vol. I. . . *April*, 1924; *Reissue*, 1927
Vol. II. . . . . . *April*, 1927

Made in Great Britain

PREFACE TO VOLUME II.

In the preface to the first volume it was stated that the remarkable advances in the science of Spectroscopy since 1913 had rendered it necessary to subdivide the original single volume of this book into two. Very soon after the publication of the first of these volumes it became evident that even this amount of subdivision was quite insufficient to permit of a reasonably full account being given of the more modern developments of the subject. The advent of the Bohr theory of spectra has had an influence on spectroscopy which can only be described as profound. Not only has the science been placed on a sound mathematical basis and emission spectra found a clear and convincing explanation, but the phenomena of the Zeeman effect and the Stark effect have also been explained in a singularly elegant manner. In addition to this a stimulus has been given to investigation which has resulted in discoveries of signal importance in fields that are closely allied to the main principles of the science.

In order to permit of these many advances being reviewed it has been found necessary to subdivide the whole book into four volumes. In this second volume will be found an account of the work on interferometer methods, together with chapters on the methods of illumination, the nature of spectra, fluorescence and phosphorescence, and the photography of the spectrum. The third volume will contain chapters on spectral series, the Zeeman effect, the Stark effect, and emission band spectra, whilst the fourth volume will deal in the main with absorption spectra, and the shift of spectrum lines caused by pressure and by motion in the line of sight. This subdivision has the advantage that the more direct applications of the Bohr theory will be discussed in one volume, namely the third.

I wish once again to express my great indebtedness to those who have given me invaluable assistance. To my friend Dr. C. E. K. Mees of the Eastman Kodak Company I render my

deep thanks for his article on the methods of sensitising photographic plates to the red and extreme ultra-violet. I thank, too, those many other friends who combined to make my journey through America in 1924 so happy and helpful a one, and, in particular, Dr. Hale and Director Adams and his colleagues on the staff of the Mount Wilson Observatory for their stimulating encouragement during my all too brief visit. Once again I owe a great debt to Miss E. E. Kelly for her untiring assistance, so willingly rendered and so helpful in lightening my work.

To the proprietors of many publications I express my cordial thanks for permission to reproduce many of the illustrations in this volume. I have acknowledged these in the majority of cases in the text, but in the case of the Astrophysical Journal the excerpts have been too many to acknowledge specifically on each occasion. This standard journal of Spectroscopy occupies a position that is unique, and the least that I can do is to express to the Editors and Proprietors not only my indebtedness for the permission, so freely given, to reproduce many illustrations, but also, in common with other spectroscopists and with astronomers, my appreciation of the great work they are doing on behalf of spectroscopic science.

E. C. C. B.

CONTENTS.

CHAPTER I.

PAGE

APPLICATION OF INTERFERENCE METHODS TO SPECTROSCOPY . 1

The Michelson interferometer, 2. The measurement of the structure of spectrum lines, 9. Determination of the absolute wave-length of the cadmium lines, 10. The Fabry and Perot interferometer and determination of wave-lengths, 11. The periodic error in Rowland's standard map of the solar spectrum, 34. The determination of secondary wave-length standards, 36. The correction for change of phase on reflection, 39. The application of the Fabry and Perot and Michelson interferometers to astronomy, 44. The Lummer-Gehrcke and Barnes interferometer plates, 53.

CHAPTER II.

METHODS OF ILLUMINATION 55

Introduction, 55. Flame spectra, 56. Band spectra given by flames, 60. King's work on electric resistance furnace spectra, 62. Temperature classification of spectrum lines, 71. The absorption spectra of metallic vapours, 76. The effect of temperature on the absorptive and emissive powers of metallic vapours, 79. Band spectra in the electric furnace, 85. The explosion of wires, 86. Arc spectra, 90. The Pfund arc, 92. The vacuum arc, 95. The mercury vapour lamp, 97. The transparency of quartz to ultra-violet rays and its deterioration, 101. The Mount Wilson classification of the iron lines, 103. The pole effect, 108. Spark spectra, 112. The construction of condensers, 113. Spark spectra of solutions, 119. The electric spark in a vacuum, 124. The arc and spark discharge in liquids, 128. Enhanced lines, 132. Quantitative analysis by spark spectra, 134. De Gramont's ultimate lines, 148. The mechanism of the spark, 153. The spectra of gases, 157. The construction and filling of vacuum tubes, 159. Exhaust pumps, 168. The Wehnelt cathode, 172. Cathodo-luminescence spectra, 174. Electrodeless ring discharge, 175.

CHAPTER III.

THE NATURE OF SPECTRA 177

Classification of emission spectra, 177. Characteristics of spectrum lines, 178. The structure of spectrum lines, 179. The breadth of spectrum lines, 190. The length of spectrum lines, 196. Reversal of spectrum lines, 196. Plurality of spectra, 199. The elementary and secondary spectra of hydrogen, 200. Merton and Barratt's classification of the secondary hydrogen lines, 209. The separation of gases in vacuum tubes, 212. The spectra of oxygen, 213. The spectra of nitrogen, 214. The spectra of carbon, 219. The spectra of isotopes, 230.

CHAPTER IV.

PAGE

FLUORESCENCE AND PHOSPHORESCENCE 234

Introduction, 234. Stokes' law, 236. Cathodo-luminescence of minerals, 237. Resonance radiation and resonance spectra, 237. Magnetic rotation spectra, 242. Fluorescence and phosphorescence, 245. Fluorescence of gases and solutions, 246. Fluorescence of mercury vapour, 247. Fluorescence of organic compounds, 250. Experimental technique, 251. Nichols' work on the fluorescence of the uranyl salts, 256. Tesla luminescence spectra, 283. Phosphorescence, 289. The phosphoroscope and the measurement of persistence, 290. Lenard and Klatt's work on sulphide phosphores, 293. Preparation of the phosphores, 295. The spectra of the phosphorescent emission, 298. The influence of temperature, 301. Relations between the wave-lengths of the exciting and emitted radiations, 304. The influence of the diluent, 307. The decay curves of phosphorescence, 308. Cathode ray excitation of phosphorescence, 312. Experimental methods, 312. Crookes' investigations, 315. Urbain and Bruninghaus' work, 315. Phosphorescence at low temperatures, 319. Flame excitation of luminescence, 322. A theory of fluorescence and phosphorescence, 329.

CHAPTER V.

THE PHOTOGRAPHY OF THE SPECTRUM 356

Sensitisation of plates to the yellow, red, and infra-red, 357. The wedge spectrograph, 358. Comparison of dye-stuffs as sensitising agents, 362. Sensitising plates by bathing, 368. Special methods of photography in the red and infra-red, 373. Abney's process, 373. Ritz's modification, 375. The reversal method, 376. The phosphoro-photographic method, 377. The photography of the extreme ultra-violet, 378. The fluorescence method, 379. Schumann's process, 380.

AUTHOR INDEX 385

SUBJECT INDEX 392

LIST OF PLATES.

PLATE I. . . . . *To face page* 362

„ II. . . . . „ 362

„ III. . . . . „ 365

SPECTROSCOPY.

CHAPTER I.

THE APPLICATION OF INTERFERENCE METHODS TO SPECTROSCOPY.

By an interference spectroscope, or interferometer, is meant an apparatus in which a beam of light, coming from a single source, is divided into two portions, which by some means or other are caused to suffer a different amount of retardation, so that, when they are reunited, interference is produced. Michelson was the first to make use of such an apparatus in spectroscopic work, and he was thereby able to bring a much greater resolving power into play than had been possible before.

Michelson has been able to apply his interferometer to the investigation of several different problems, two of which are of outstanding importance and interest. In the first place, he applied the instrument to the study of the nature of the different radiations which are grouped together in a single spectrum line, and he examined many well-known lines which previously had been considered as being monochromatic. In this investigation he found that three of the cadmium lines are singularly pure, and this discovery led him to recognise the possibility of the measurement of the wave-lengths of these lines with a far greater accuracy than could be reached in the case of lines which are more complex. This formed the second part of Michelson's work with his interferometer, and was carried out in collaboration with Benoit. The wave-lengths were determined by direct comparison with the standard metre at Paris, and the accuracy reached was extraordinary, and, as was fully described in Vol. I., pp. 35 *et seq.*, it was agreed by the leading spectroscopists of the world that the measurement of the cadmium red ray (which is the purest of the three) shall serve as the primary standard of all wave-length measurements. By that it is meant, of course, that all measurements of the wave-lengths of lines shall be determined in terms of the cadmium red line as the fundamental standard. Michelson's first measurement of the wave-length of this line was $\lambda = 6438{\cdot}4722$ tenth metres, and subsequently Benoit, in collaboration with Fabry and Perot, introduced a small correction which reduced the wave-length and the final value adopted was—

$$\lambda = 6438{\cdot}4696\ \text{I}\,\text{Å} \text{ at } 15^\circ \text{ and } 760 \text{ mm. pressure,}$$

the value of the Ångström unit on the international standard being thus defined.

It has now become an integral part of spectroscopic history how Fabry and Perot succeeded in devising an interferometer whereby they compared directly the wave-lengths of many solar and iron lines with the cadmium standard, and how they proved that the Rowland standard map of the solar spectrum had not the accuracy which had been previously attributed to it. This discovery, coupled with Kayser's proof that the method of wave-length determination by the method of coincidence of the different orders of spectra obtained with the grating is unreliable, initiated a very drastic change in the methods of wave-length measurement. It was agreed that a system of secondary standards was to be set up consisting of wave-lengths of trustworthy lines measured by direct interferometric comparison with the cadmium standard. Further, it was agreed that a set of tertiary standard wave-lengths were to be determined by methods of interpolation.

This work, which has now reached a measure of completion, was dealt with in Vol. I., Chapter II., in the statistical sense, tables of secondary and tertiary standard wave-lengths in the spectra of iron, helium, and neon being given.

More recently Michelson has applied his interferometer to the measurement of stars, and this work, although perhaps not strictly spectroscopic, has a two-fold interest. It reveals a new and most remarkable line of investigation with this instrument, and, further, the results cannot but fascinate and enchant all who read of them.

In this chapter it is proposed to give an account of the application of interferometric methods to spectroscopy, and to follow the development of this work in the order of its progress.

A diagram of Michelson's interferometer is shown in Fig. 1.[1]

The rays from the source V pass through one or more prisms, in order to separate the various radiations from one another, and are focussed upon the slit S; in this way any particular radiation can be separately examined. The light passing through the slit is rendered parallel by the collimating lens, and falls upon the plane parallel plate G_1, which is set at an angle of 45° to the path of the light beam. The front surface of this plate is half silvered, so that a portion of the incident ray is reflected, while the remainder passes through the plate. The first portion travels to the movable plane mirror M_2, and the second to the fixed mirror M_1, both mirrors being fully silvered. These mirrors return the light to the silvered surface of G_1, where the first portion is transmitted and the second reflected, so that both portions coincide and enter the telescope E. As regards the thickness of the silver layer on G_1, Michelson remarks "that the light entering the telescope is a maximum, when the thickness of the silver film is such that the intensity of the transmitted light is equal to that of the reflected light.

[1] *Phil. Mag.* (5), **34**, 200 (1892).

The silvering has another important advantage, in diminishing the relative intensity of the light reflected from the other surface. Indeed, for this purpose it is advisable to make the film heavier, even so thick that the reflected light is twice as bright as the transmitted. This does not affect the ultimate ratio of intensities of the interfering pencils, for what is lost by transmission on entering the plate G_1 is made up by reflection on leaving it, the effect being simply to diminish somewhat the whole intensity. Another advantage of the thicker film is that it can be made uniform with far less difficulty than the thin film."

The two mirrors are provided with screws for purposes of adjustment, and M_2 is mounted on a sliding carriage, which is moved by a micrometer screw of 1 mm. pitch. The pencil of rays, which is in the

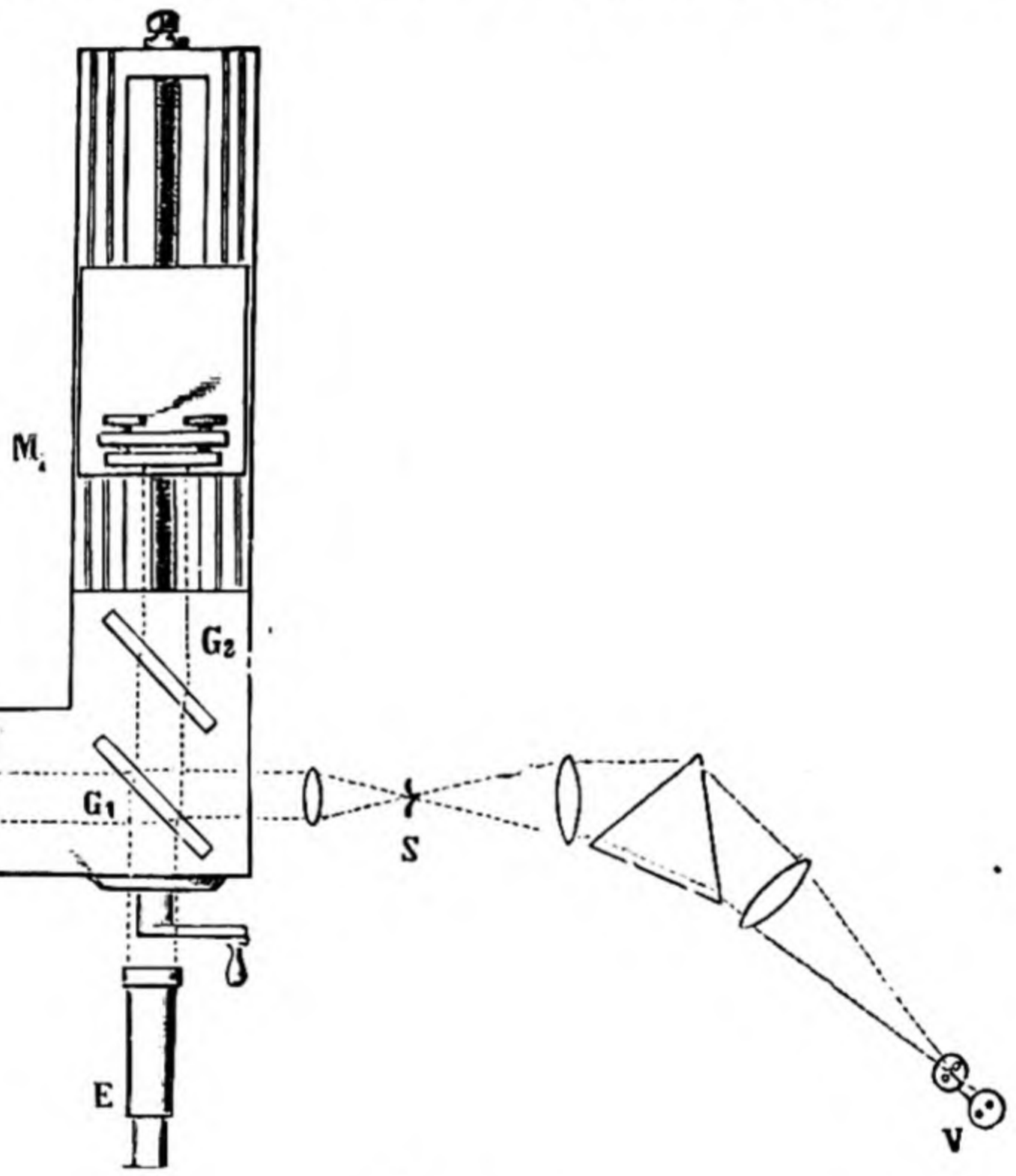


FIG. 1.

first place transmitted by the silver layer on G_1, as will be seen, passes three times through the plate G_1; an exactly similar plate, G_2, is placed at an angle of 45° in the path of the other pencil in order to compensate for the retardation thus caused.

Now, if there be no difference in path travelled by the two pencils, *i.e.* if the distances from the silver layer to the two mirrors be equal, there will be no interference. If, however, a small difference be introduced by the moving of M_2, then interference fringes will be seen in the telescope as a series of concentric circles. These fringes are produced in exactly the same way as by a film or plate of air between two plane surfaces; in other words, they are the same phenomenon as Newton's rings.

Michelson gave the theory of these interference bands,[1] and showed that the position of maximum distinctness is given by the formula—

$$P = \frac{t_0}{\tan \phi} \tan i \cos^2 \theta,$$

where P is the distance of the plane of maximum distinctness from the mirrors, t_0 the thickness of the equivalent air plate where it is cut by the axis of the telescope, ϕ the inclination of the two surfaces, and θ and i the components of the angle of incidence parallel and perpendicular to the intersection of the surfaces.

If, now, θ be small, the variation of P with θ may be neglected, and therefore—

$$P = \frac{t_0}{\tan \phi} \tan i,$$

or, with sufficient accuracy—

$$P = \frac{t_0}{\phi} i.$$

The focal plane, therefore, varies very rapidly with i, so that, unless $\phi = 0$, it is impossible to see all parts of the interference bands with equal distinctness.

Putting $\phi = 0$, that is, making the surfaces truly parallel, then $P = \infty$, so that if the bands be observed with a telescope focussed for infinity the interference fringes will be equally distinct in all parts; they will thus be concentric circles the angular diameter of which is given by—

$$\cos \theta = \frac{\Delta}{2t_0},$$

where Δ is the difference in path between the two pencils. If instead of Δ we put $2t_0 - n\lambda$, and for $\cos \theta$ its approximate value $1 - \frac{\theta^2}{2}$,

then

$$\theta_n = \sqrt{\frac{n\lambda}{t_0}}.$$

If in the above apparatus the mirror be so set that there is no difference in path between the two pencils, the illumination obtained in the telescope will, of course, be a maximum; if, now, the mirror M_2 be moved away 1 mm., a difference of path will be set up of 2 mm., and a series of fringes will be seen. Michelson [2] estimates the "visibility" of these fringes, the visibility being found from the expression $V = \frac{I_1 - I_2}{I_1 + I_2}$, where I_1 is the intensity at the centre of a bright band and I_2 the intensity at the centre of the adjoining dark band. This visibility is determined for each successive shift of the mirror M_2

[1] *Phil. Mag.* (5), **13**, 236 (1882). [2] *Ibid.*, **34**, 280 (1892).

1 mm. outwards, and the values thus obtained are plotted on a curve, the ordinates expressing visibility and the abscissæ differences of path. This visibility curve has various forms depending upon the distribution of light in the radiation examined, and the actual structure of the spectrum " line " can be elucidated by studying the curve obtained.

Before, however, proceeding to discuss the shapes of the visibility curves, it may be pointed out that Michelson drew up a table of corrections to be applied to the visually estimated values, in order to reduce them to the true values, *i.e.* a table of corrections for personal error. This was done in the following way: An apparatus was set up in which interference bands were produced, and in which the two values I_1 and I_2 could be obtained from the constants of the apparatus. The values were also observed and estimated; by comparing the values obtained for the visibility by the two methods, the personal error could be determined.

Two quartz lenses, one concave and the other convex, but of equal curvatures, were mounted with their crystalline axes at right angles to each other between two Nicols. Under these conditions a series of concentric interference rings appeared. If α be the angle between the principal section of the polariser and the axis of the first quartz, and ω the angle between the axis of the second quartz and the analyser, the intensity of the light transmitted will be—

$$I = \cos^2(\omega - \alpha) - \sin 2\alpha \sin 2\omega \sin^2 \pi \frac{k(t_1 - t_2)}{\lambda},$$

where t_1 is the thickness through the first quartz, and t_2 that through the second. If the analyser and polariser are parallel, then $\omega = \alpha$,

and
$$I = 1 - \sin^2 2\alpha \sin^2 \pi \frac{k(t_1 - t_2)}{\lambda};$$

whence
$$I_1 = 1, \text{ and } I_2 = 1 - \sin^2 2\alpha,$$

and
$$V = \frac{I_1 - I_2}{I_1 + I_2} = \frac{1 - \cos^2 2\alpha}{1 + \cos^2 2\alpha}.$$

The visibility of the fringes in this apparatus was observed and estimated for all values of α, and was also calculated from the expression $\frac{1 - \cos^2 2\alpha}{1 + \cos^2 2\alpha}$; both sets of values were plotted against the values of α. The two curves differed in shape slightly, and a table of corrections was drawn up which was to be applied to all estimations of visibility, in order to correct the personal error in assessment of the intensities and to reduce them to the true values. These corrected values were used for the visibility curves.

The interpretation of these visibility curves is based on the following :—[1]

[1] *Phil. Mag.* (5), **31**, 338 (1891).

Michelson first showed that the visibility is given by—

$$V^2 = \frac{S^2 + C^2}{P^2},$$

where $P = \int \phi(x)dx,$

$C = \int \phi(x) \cos 2\pi D x dx,$

and $S = \int \phi(x) \sin 2\pi D x dx.$

In these expressions D is the difference in path between the two pencils, and $\phi(x)$ is the distribution of intensity in the source, that is to say, in the radiation examined. By $\phi(x)$ is meant the curve of intensity in the spectrum line with abscissa x in oscillation frequencies and ordinate some function of x. In Fig. 2 is shown such an intensity curve of a spectrum line; the abscissæ x are expressed in oscillation frequencies, and it will be noticed that they are measured from the centre of the line. The function of x expressed upon the ordinates is $e^{-0.013x^2}$, where e is the base of natural logarithms. Now, Michelson introduced various values of $\phi(x)$ into the above expressions, and calculated the value of the visibility. As, however, the actual experimental observations only agreed with the distribution of intensity as given by Maxwell's law, we will only discuss this particular case. The distribution of intensity is given by this law to be $\phi(x) = e^{-\frac{x^2}{a^2}}$, which is expressed graphically in Fig. 2.

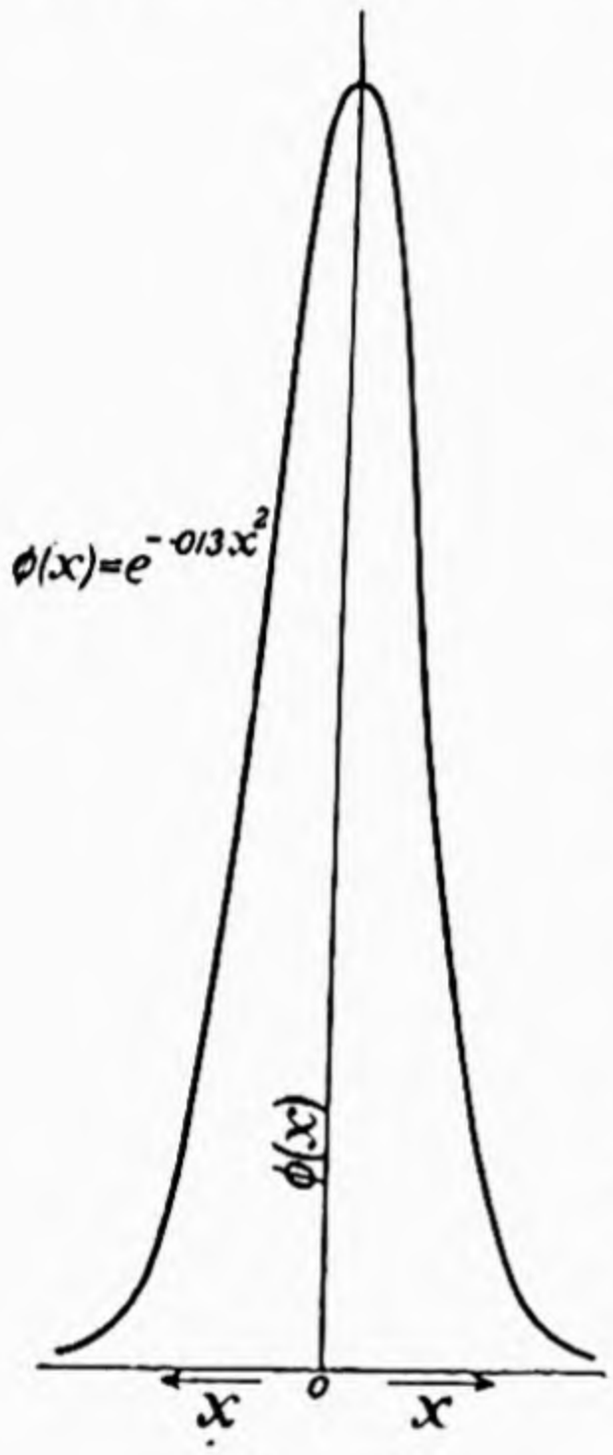


FIG. 2.

It must be remembered that in the expressions for P, C, and S given above the limits of integration are of course the limits of the illumination; if, now, the illumination be perfectly symmetrical, as shown in Fig. 2, then clearly S vanishes, and we have therefore—

$$V = \frac{C}{P}.$$

Now, Michelson at first assumed the symmetrical distribution of intensity, and afterwards found that this was justified.

If, now, Δ be the extreme difference in wave-length of the radiations in question, and Δ_0 the smallest difference that can be resolved by a grating having as many lines, N, as there are wave-lengths in the difference of path,

then $$\Delta = \lambda_1 - \lambda_2,$$

where λ_1 and λ_2 are the wave-lengths of the extreme rays. If we put the difference in frequency between these rays $= a$, then we have—

$$a = \frac{1}{\lambda_2} - \frac{1}{\lambda_1} = \frac{\lambda_1 - \lambda_2}{\lambda^2},$$

if $\lambda =$ the mean of λ_1 and λ_2.[1]

Therefore $$\Delta = \lambda_1 - \lambda_2 = a\lambda^2.$$

Again $$\frac{\lambda}{\Delta_0} = \mathrm{N}, \text{ and thus } \Delta_0 = \frac{\lambda}{\mathrm{N}},$$

therefore $$\frac{\Delta}{\Delta_0} = \frac{a\lambda^2}{\frac{\lambda}{\mathrm{N}}} = a\mathrm{D},$$

where D, as above, $= \mathrm{N}\lambda =$ the difference in path. The ratio $\frac{\Delta}{\Delta_0}$ is denoted in the following by the letter n.

Amongst the several values used by Michelson for $\phi(x)$ in the calculation of the visibility curves, the most important is—

$$\phi(x) = e^{-p\frac{x^2}{a^2}},$$

which is the distribution resulting from Maxwell's law. The visibility curve is then given by—

$$\mathrm{V} = e^{-\frac{\pi^2 n^2}{p}},$$

which is not periodic.

If there are two sources, then Michelson shows that the visibility is given by—

$$\mathrm{V}_2^2 = \frac{1 + r^2 + 2r\cos 2\pi\frac{\mathrm{X}}{\mathrm{D}}}{1 + 2r + r^2}\mathrm{V}^2,$$

where r is the ratio of intensities in the two sources, X is the abscissa of the visibility curve, that is to say, the difference in path, and D the period of the curve, which is inversely proportional to the distance between the components.

If, now, as before,

$$\phi(x) = e^{-p\frac{x^2}{a^2}},$$

then we have $\mathrm{V}_2 = e^{-\frac{\pi^2 n^2}{p}}\sqrt{\frac{1 + r^2 + 2r\cos 2\pi\frac{\mathrm{X}}{\mathrm{D}}}{1 + 2r + r^2}}$.

Michelson now considers the "half-width" of the spectrum line; by the "half-width" is meant the value of x when $\phi(x) = \frac{1}{2}$. It must be remembered that $\phi(x)$ represents the curve of distribution of intensity in the line obtained by putting the values of the oscillation frequency on the abscissæ and those of $\phi(x)$ on the ordinates. The values of x are measured from the centre of the line, and therefore the

[1] Strictly speaking, the geometric mean.

true practical width of the line is about four times the "half-width." If we put δ equal to the half-width we then have—

$$\delta = x \text{ when } \phi(x) = \tfrac{1}{2}, \text{ that is to say, when } e^{-p\frac{\delta^2}{a^2}} = \tfrac{1}{2}.$$

Now,
$$e^{-p\frac{x^2}{a^2}} = e^{-p\frac{\delta^2}{a^2}\times\frac{x^2}{\delta^2}} = \left(e^{-p\frac{\delta^2}{a^2}}\right)^{\frac{x^2}{\delta^2}} = (\tfrac{1}{2})^{\frac{x^2}{\delta^2}},$$

or
$$\phi(x) = 2^{-\frac{x^2}{\delta^2}}.$$

We have already seen that $V = e^{-\frac{\pi^2 n^2}{p}}$,

but
$$n = aX,$$

therefore
$$V = e^{-\frac{\pi^2 a^2 X^2}{p}}.$$

Now, as above,
$$e^{-\frac{p\delta^2}{a^2}} = \tfrac{1}{2},$$

therefore
$$\frac{p\delta^2}{a^2} = \log_e 2,$$

and
$$\frac{a^2}{p} = \frac{\delta^2}{\log_e 2}.$$

Substituting this in the expression for V, we have—

$$V = e^{-\frac{\pi^2\delta^2 X^2}{\log_e 2}}.$$

Again, if we put Δ for X when $V = \tfrac{1}{2}$, that is, let Δ be the value or the abscissa of the visibility curve when $V = \tfrac{1}{2}$,

then
$$e^{-\frac{\pi^2\Delta^2\delta^2}{\log_e 2}} = \tfrac{1}{2},$$

and
$$-\log_e 2 = -\frac{\pi^2\Delta^2\delta^2}{\log_e 2}.$$

Thus
$$\log_e 2 = \pi\Delta\delta,$$

and
$$\delta = \frac{\log_e 2}{\pi\Delta} = \frac{0{\cdot}22}{\Delta} \text{ very nearly.}$$

This expression gives the value of the half-width in terms of oscillation frequencies; in order to convert into wave-lengths δ must be multiplied by λ^2.[1]

[1] If the width of a line in oscillation frequencies $= \frac{1}{\lambda_1} - \frac{1}{\lambda_2} = \frac{\lambda_2 - \lambda_1}{\lambda^2}$, while the width of the same line in wave-lengths $= \lambda_2 - \lambda_1$, therefore to convert the former into the latter it must be multiplied by λ^2. This is not strictly true; λ is really the geometric mean of λ_1 and λ_2.

Substituting $\frac{\log_e 2}{\pi\Delta}$ for δ in the equation—

$$V = e^{-\frac{\pi^2 X^2 \delta^2}{\log_e 2}},$$

we have

$$V = e^{-\frac{X^2 \log_e 2}{\Delta^2}}$$

$$= \left(2^{\frac{1}{\log_e 2}}\right)^{-\frac{X^2}{\Delta^2}}$$

$$= 2^{-\frac{X^2}{\Delta^2}}$$

Therefore the equation for two sources in which the intensity is distributed according to Maxwell's law is given by—

$$V_2 = 2^{-\frac{X^2}{\Delta^2}} \cos \frac{r}{D},$$

where the symbol $\cos \frac{r}{D}$ is put for the expression—

$$\sqrt{\frac{1 + r^2 + 2r \cos 2\pi \frac{X}{D}}{1 + r^2 + 2r}}.$$

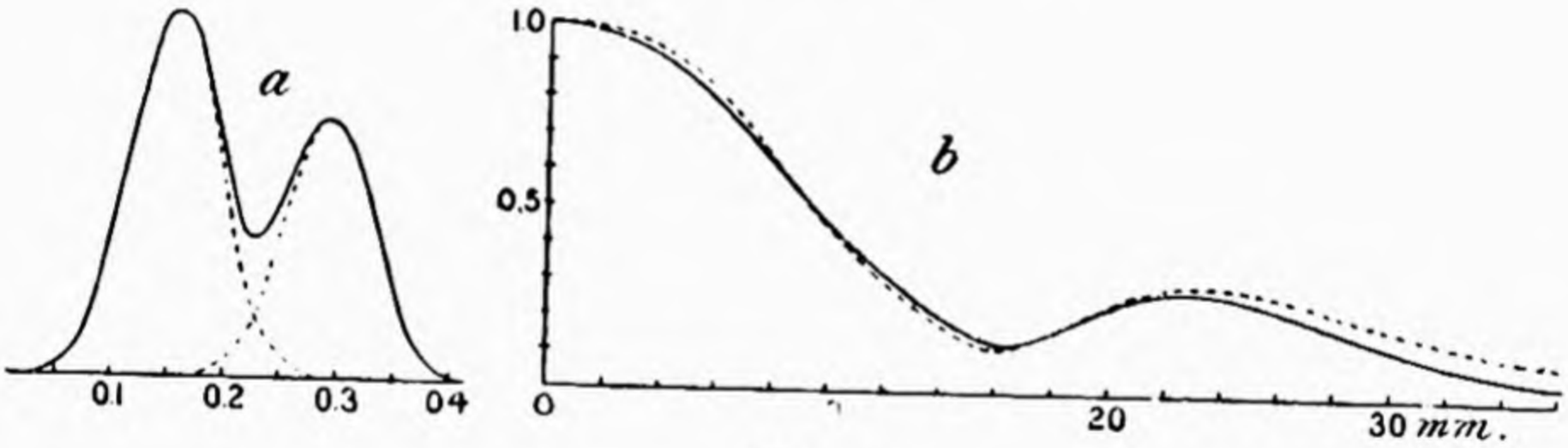


FIG. 3.

Michelson then applied these theoretical considerations to actual observations. He plotted the visibility curves for the radiations from different elements, most of which were excited by electric discharge in vacuo. In the case of the metals a vacuum tube containing some of the substance was placed in a box which was heated just sufficiently for the electric discharge to pass freely and to give a steady light, when the temperature was kept as steady as possible. The visual observations of the visibility were corrected for personal error from the curve of errors previously described, and when the visibility curve was drawn, a formula was found to express it as closely as possible, from which the distribution of intensity in the radiation was obtained.

The visibility curve of the red hydrogen line is shown in the full curve in Fig. 3 (*b*); the dotted curve represents—

$$V = 2^{-\frac{X^2}{19^2}} \cos \frac{0{\cdot}7}{30}$$

The visibility curve is therefore practically the same as that calculated for a double source the ratio of brightness of which is equal to 0·7.

Now, D in the formula for V, or the period of the curve, is inversely proportional to the distance between the components of the pair of lines, this distance being measured as hitherto in oscillation frequencies. We may therefore put the distance between the wave-lengths of the two lines equal to $\frac{\lambda^2}{D}$. The formula for the hydrogen red line gives D = 30, and as $\lambda = 6{\cdot}56 \times 10^{-4}$ mm., we have for the separation of the two components—

$$\frac{(6{\cdot}56 \times 10^{-4})^2}{30} = 0{\cdot}14 \text{ A.U.}$$

Again, the formula gives $\Delta = 19$, whence we find that—

$$\delta = 0{\cdot}0115, \text{ or } 0{\cdot}049 \text{ in Ångström units.}$$

Therefore the half-width of each component is 0·049 A.U. From these data the curves in Fig. 3 (*a*) were drawn, the full curve showing the distribution of the intensity.

Similarly for the blue hydrogen line the equation of the visibility curve was found to be—

$$V = 2^{-\frac{X^2}{24^2}} \cos \frac{0{\cdot}7}{28},$$

so that here again is a double line with 10 : 7 as the ratio of intensity of the components, $\lambda_1 - \lambda_2 = 0{\cdot}08$ A.U. and $\delta = 0{\cdot}057$ A.U.

The radiations from oxygen, sodium, zinc, cadmium, thallium, and mercury were also examined, and in many cases, notably that of the mercury green line, the sources were found to be very complex. The visibility curves of the mercury line are shown in Fig. 4, with the probable intensity curves of the radiations.

The cadmium lines were especially interesting on account of their narrowness. The curve of the red line at $\lambda = 6439$ agreed extremely well with the simple exponential curve—

$$V = 2^{-\frac{X^2}{138^2}}.$$

This line is evidently, therefore, a single line with half-width = 0·0065.

The green line at 5086 was found to be a close double, the intensity of the components being in the ratio of 5 to 1 ; their distance apart is 0·022, and the half-width of each is 0·0048, in Ångström units.

Michelson and Benoit applied this interferometer to the determination of the length of the standard metre in terms of the wave-lengths of the cadmium lines,[1] these rays especially being chosen on account of their width being so small ; they were found to be the most homogeneous of any rays examined. A description of the method would take up too much space, and it must suffice to give the final results obtained in air at 0° and 760 mm. pressure :—

[1] *Mém. du Bureau internat. des poids et mésures*, II, 1 (1895).

Red line, 1 metre = 1553163·5 λ, $\therefore \lambda$ = 6438·4722 tenth metres.
Green line, 1 ,, = 1900249·7 λ, $\therefore \lambda$ = 5085·8240 ,, ,,
Blue line, 1 ,, = 2083372·1 λ, $\therefore \lambda$ = 4799·9107 ,, ,,

In the two last cases the principal component was measured. These values were the original ones published by Michelson and Benoit and, as was shown in Vol. I., p. 35, they are considerably smaller than those determined by Rowland. In view of the doublet character of the green and blue lines the red line was finally adopted by spectroscopists as the primary standard, with the wave-length $\lambda = 6438{\cdot}4696$ in air at 15° and 760 mm.

Reference may be made here to the use of Michelson's interferometer in analysing infra-red radiations by Rubens and Hollnagel. This was described in Vol. I., p. 231.

Following on Michelson's work, Fabry and Perot have applied interference methods to spectroscopy, and have devised an apparatus by means of which observations can be made with beautiful simplicity. The principle of Fabry and Perot's apparatus consists in the use of a film or layer of air enclosed between two plane parallel plates of glass. These two plates are half silvered on the inner sides, and set parallel to one another. The interference phenomena are obtained by allowing a beam of monochromatic light to pass through at normal incidence, and the fringes are observed in a telescope.

If a source of monochromatic light be examined through a thin layer of air enclosed between two parallel surfaces of glass a series of rather confused fringes will be seen on a uniformly illuminated background. It is clear that these fringes are produced by the interference between those rays which pass directly through the apparatus, *e.g.* the ray A (Fig. 5), and those which undergo double reflection, *e.g.* the ray B. After the ray B has been twice reflected, of course a small portion will undergo a further double reflection; the intensities of this and of the multiple reflections generally, in the case of plain glass surfaces, are so small as to have no material influence. If f is the reflecting power of the glass[1] the relation between the minimum and maximum intensities of the fringes produced is given by the expression—

$$\rho = \left(\frac{1 - f}{1 + f}\right)^2.$$

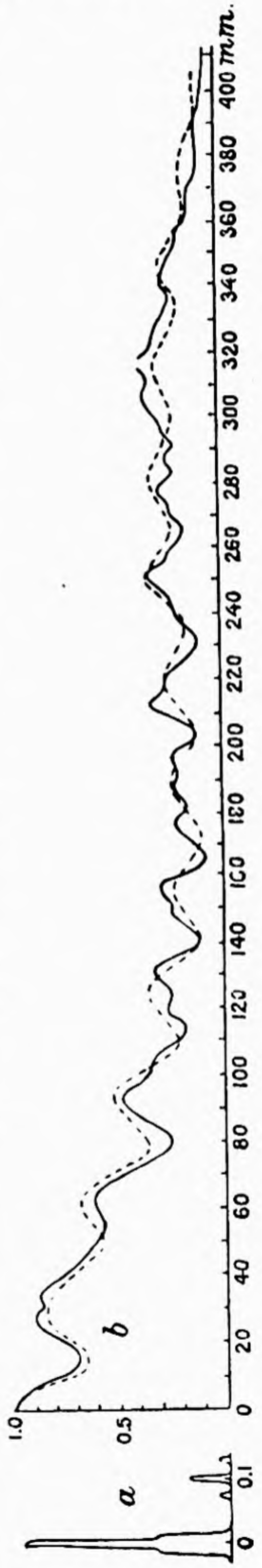


FIG. 4.

[1] *Ann. Chim. et Phys.*, **12**, 459 (1897).

With a glass having an index of refraction of 1·52, the value of f at normal incidence is equal to 0·042, whence $\rho = 0{\cdot}84$. There is thus but little difference between the intensity of the maxima and minima.

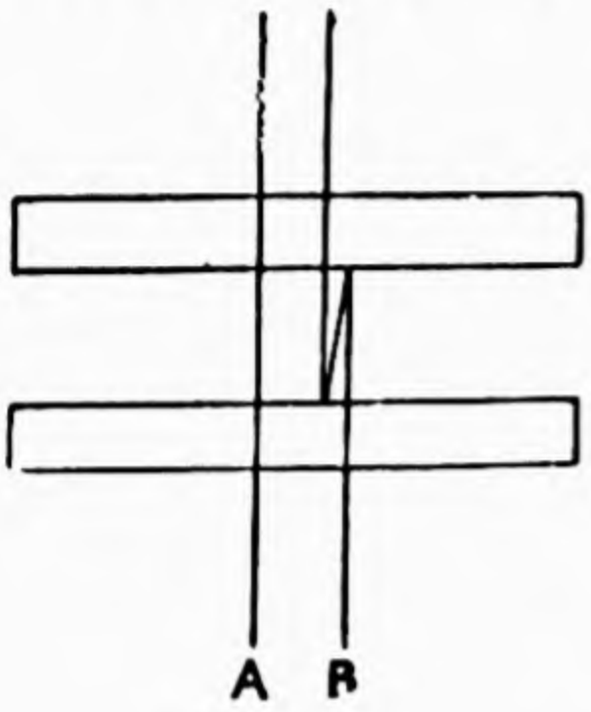


FIG. 5.

If now by slightly silvering the surfaces the reflecting power be increased, the phenomena will present quite a different appearance. If, for example, $f = 0{\cdot}74$, then ρ is reduced to 0·02, that is to say, the minima become almost absolutely black. Further, the fringes are to be seen as very narrow brilliant lines separated by wide dark intervals. This effect is due to the multiple reflections, which become of considerable importance now that the reflecting power is increased, and it is necessary in dealing with the rays emerging from the apparatus to consider the interference which takes place between the rays directly transmitted and those which have undergone 2, 4, 6, etc., reflections. The fringes seen are due to the superposition of all these rays.

If Δ be the difference of path between the direct ray and the ray which has been twice reflected, then the successive rays will differ in their paths from the direct ray by Δ, 2Δ, 3Δ, and so on; their intensities will decrease, but not very rapidly. If Δ be a round number of wave-lengths, *i.e.* if $\frac{\Delta}{\lambda}$ be a whole number, all the waves will agree in phase, and there will be a maximum of intensity; but if $\frac{\Delta}{\lambda}$ differ a very little from a whole number, then amongst the successively reflected rays there will be found one which will differ very much in phase from the direct ray, and will thus considerably detract from the intensity; and therefore it follows that the higher the value of f, the smaller is the change necessary in $\frac{\Delta}{\lambda}$ from a whole number in order to produce a considerable decrease in the intensity. This is due to the fact that the more f increases, the greater is the effect of the multiple reflections.

Fabry and Perot give a rigid proof of this, and show that if, again, f be the reflecting power of each silvered surface, θ the fraction of the incident light each face allows to pass through, and Δ the difference in path between the direct and twice reflected rays, then the intensity will be given by—

$$I = \frac{\theta^2}{(1-f)^2} \times \frac{1}{1 + \frac{4f}{(1-f)^2}\sin^2 \pi\frac{\Delta}{\lambda}}.$$

Considering the second factor on the right-hand side, and putting $f = 0{\cdot}75$, then this factor becomes equal to—

$$\frac{1}{1 + 48 \sin^2 \pi \frac{\Delta}{\lambda}}.$$

When, therefore, $\frac{\Delta}{\lambda}$ is a whole number, this factor is equal to unity, and the intensity reaches a maximum of $\frac{\theta^2}{(1-f)^2}$; but if $\frac{\Delta}{\lambda}$ differs from a whole number, the above second factor becomes rapidly smaller than unity; and thus with a small change in $\frac{\Delta}{\lambda}$ from a whole number a great decrease in intensity is produced. In other words, close on each side of a maximum the intensity falls very rapidly to almost zero, and the maxima are therefore very sharply defined. At the distance of one-tenth of a fringe from the maximum the intensity falls to one-sixth of the maximum.

The definition of the bright fringes thus depends directly upon f, but it must be remembered that as f is made greater, the absorption of light by the films increases, and therefore the whole quantity of light passing through the apparatus is diminished. The fact of this absorption limits the thickness of the silver films; in practice the thickness should depend upon the intensity of the light to be employed. The best process for silvering is that given by Martin.[1] By addition of water the strength of the solutions can be varied so as to give anything from a thin veiling to an almost opaque coating. The two plates should be silvered in the same bath in order to produce the same thickness of layer on each.

The appearance of the fringes depends absolutely upon the shape of the limiting surfaces of the layer of air, since each fringe defines the points of equal thickness of the air layer. With a beam of monochromatic light at normal incidence one series of very narrow fringes will be formed; these fringes are localised in the air layer, and are thus rectilinear when the glass surfaces are plane but not parallel, and they are circular when the surfaces are slightly convex or concave. The best way to obtain them is to adjust two optically plane silvered glass surfaces until they are perfectly parallel, and then to observe the fringes with a telescope focussed for parallel rays. A complete system of rings is then obtained, of which, probably, only a small section can be seen at one time in the telescope.

If, now, instead of monochromatic light, light consisting of two different radiations be examined through the interference apparatus, two systems of fringes will be seen, the first due to one radiation and the second due to the other. If the two radiations differ in colour, then the two systems of fringes will be easily distinguishable by their appearance, and also by the different intervals between two

[1] See Appendix to Vol. IV.

consecutive fringes in the two systems; for the greater the wave-length of a ray the wider apart are the fringes it produces.

Let us put the wave-lengths of the two radiations as equal to λ_1 and λ_2, and let also $\lambda_1 > \lambda_2$. If e be the thickness of the air layer, then there will be a maximum for the ray λ_1 when $e = k_1\frac{\lambda_1}{2}$, k_1 being some whole number which represents the number of the order of the fringe. In the same way there will be a maximum for the ray λ_2 when $e = k_2\frac{\lambda_2}{2}$, k_2 also being some whole number. If the two silvered surfaces are put in contact and then slowly separated, keeping them perfectly parallel, the two systems of fringes will be comparable to two scales, the divisions of which mark the thicknesses of the layer, which are multiples of $\frac{\lambda_1}{2}$ and $\frac{\lambda_2}{2}$ respectively. The appearance of the fringes in the telescope at very small thicknesses is that the fringes of the two systems are not properly separated from one another, and as the thickness of the layer increases and the fringes cross the field of view the fringes belonging to the two systems become more separated, until a region is reached when a fringe from one ray is situated exactly between two fringes from the other ray. After this point the fringes of the two systems get closer together, until two quite, or very nearly, coincide. After this they become wider apart, and then closer together again, and so on.

The first coincidence between a fringe of the one system and a fringe of the other is when $k_2 = k_1 + 1$.

Then $$2e = k_1\lambda_1 = (k_1 + 1)\lambda_2$$

and $$k_1 = \frac{\lambda_2}{\lambda_1 - \lambda_2}.$$

The second coincidence takes place when $k_1 = 2\frac{\lambda_2}{\lambda_1 - \lambda_2}$, and, generally, the fringes coincide when—

$$k_1 = n\frac{\lambda_2}{\lambda_1 - \lambda_2}.$$

Evidently, therefore, the nearer λ_1 and λ_2 are together, *i.e.* the nearer the two rays are in the spectrum, the greater are the intervals between the coincidences. For example, with the D rays of sodium for the first coincidence—

$$k_1 = 1000 \text{ nearly},$$

that is to say, at about the thousandth fringe there will be a coincidence. These coincidences occur much more frequently with rays which differ considerably in wave-length. It must be noted that these coincidences are by no means always exact; in fact, they rarely are more than approximate. In Fig. 6 are shown one exact and one approximate coincidence. This is a diagram of the appearance given

by superposition of the D lines of sodium and the red line of lithium. It must be remembered that each fringe, in fact, forms a complete ring; in the figure only a small section is shown in order to avoid unnecessary complication. Fig. 7 shows the actual appearance of some of the fringes. Evidently, now, the closer the two rays are

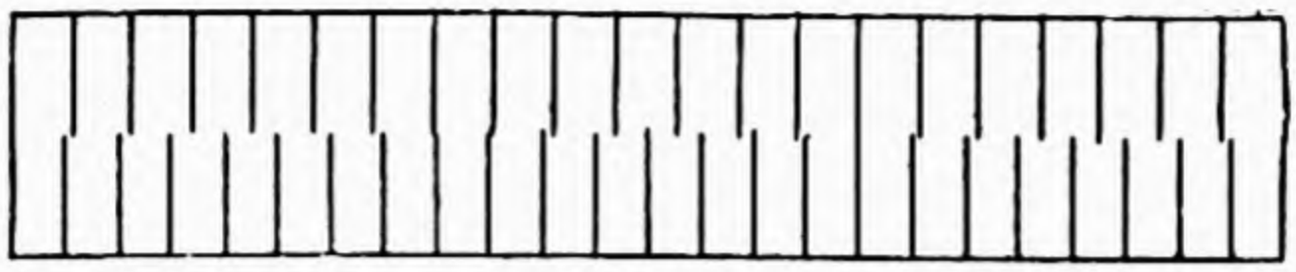


FIG. 6.

together in the spectrum, the higher will be the value of k_1 at which the first coincidence takes place, and, as we can make use of very high orders of interference in this apparatus, very closely situated rays can be separated. In other words, enormous resolving power can be applied in this way to the examination of radiations, and thus the structure of spectrum lines can readily be investigated.

Let us consider again the apparatus to be illuminated by two rays closely situated together, of wave-lengths λ and $\lambda + \epsilon$, and let Δ, the difference of path, $= 2e$; then the pth fringe of the first ray corresponds to $\Delta = p\lambda$, and the pth fringe of the second ray corresponds to $\Delta = p(\lambda + \epsilon)$. If p be very small, the two sets of fringes will not appear separated; but as p increases, the fringes will appear to double themselves and to give two sets of fringes, one belonging to one radiation and one to the other. The fringe from the ray having the greater wave-length will appear on the side corresponding to an increased length of path. In the case of the D rays of sodium we have $\frac{\epsilon}{\lambda} = 10^{-3}$, and

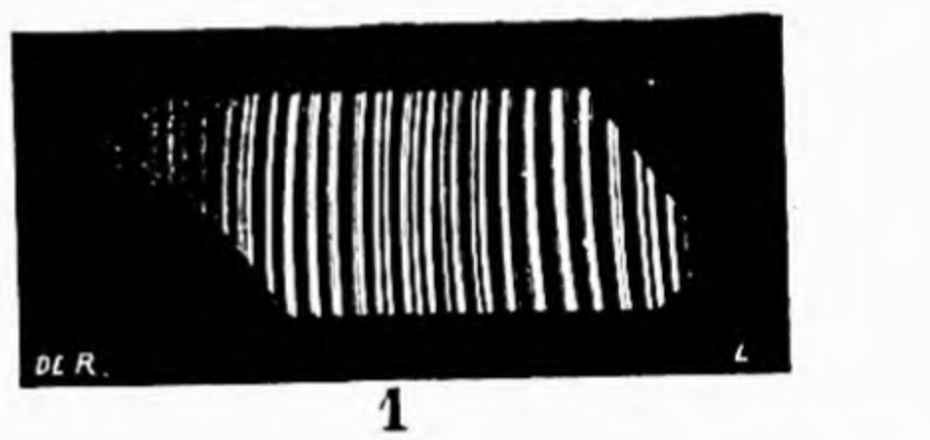


FIG. 7.

we find the doubling to be quite plain when we reach the two-hundredth fringe, for then the distance between the components is one-fifth of the interval between two successive fringes. Generally speaking, therefore, at the pth fringe we can separate two rays, for which

$$\frac{\epsilon}{\lambda} = \frac{1}{5p}.$$

Thus with an air layer 5 cm. thick ($\Delta = 10$ cm.) and $\lambda = 5000$ A.U., $p = 200{,}000$, and therefore rays can be separated for which $\frac{\epsilon}{\lambda} = 10^{-6}$; that is, rays differing in wave-length by 0·005 A.U.

It is easy to calculate the difference in wave-length of two radiations which are examined in the above way. The relative value is best found, namely, $\frac{\epsilon}{\lambda}$, which corresponds to the limit of resolution (Rayleigh).[1] In order to do this the apparatus is illuminated with the required rays, and the air layer slowly widened until the two sets of fringes are seen clearly separated, and until the fringes belonging to one radiation are exactly situated in the centre between the fringes belonging to the other radiation. This condition can at once be seen by the eye; we then have the pth fringe of the rays of wave-length $\lambda + \epsilon$ exactly situated in the centre between the pth and the $(p + 1)$th fringes of the rays of wave-length λ.

The pth fringe of the rays λ then corresponds to the difference of path Δ, and the pth fringe of the rays $\lambda + \epsilon$ corresponds to the difference $\Delta + \frac{\lambda}{2}$.

Then
$$p = \frac{\Delta}{\lambda} = \frac{\Delta + \frac{\lambda}{2}}{\Delta + \epsilon},$$

and
$$\frac{\epsilon}{\lambda} = \frac{\lambda}{2\Delta} = \frac{1}{2p}.$$

If, therefore, we know Δ or p and λ, we can calculate $\frac{\epsilon}{\lambda}$. Let us imagine now that the air layer be still further increased little by little; the two systems of fringes will then get closer together until they coincide; this takes place when Δ is twice what it was before. If Δ be increased to three times its first value, there will again be observed the first condition, which may be called the condition of complete disagreement.

Now, it may easily be seen that,[2] if the beam of light fall upon the air layer at an angle of incidence i, and e be the thickness of the layer,

then
$$\Delta = 2e \cos i.$$

A small correction has, in fact, to be added here, but, as it does not concern the present case, its consideration may be postponed. If the beam of light be truly parallel and normal to the layer, then $i = o$ and $\Delta = 2e$. This method is convenient in cases when e is small, and therefore small errors in parallelism have little influence; but when e becomes very large, a very small error in parallelism produces confusion in the fringes. Under these circumstances it is always pref-

[1] See Vol. I., p. 63.

[2] *Ann. Chim. et Phys.*, **16**, 115 (1899).

erable to work with a slightly convergent beam of light, and observe the fringes with a telescope focussed for parallel rays. At each point of the field there will be found a single value of i, and thus one single value of Δ, so that perfect clearness of fringes will be obtained. As the angular field of the telescope is very small and i thus small, we may put—

$$\Delta = 2e\left(1 - \frac{i^2}{2}\right)$$
$$= 2e - ei^2;$$

Δ therefore decreases with increasing values of i, and is therefore a maximum in the centre of the field. The fringes are therefore to be seen as rings centred round the axis of the beam of light, and the effect of increasing e is to cause the ring to expand. In observing these fringes, therefore, it must be remembered that in the system of fringes seen in the telescope field any one fringe corresponds to a smaller difference of path than does the next fringe nearer the centre. If the fringe nearest the centre were the pth of a series, then the next fringe, counting from the centre, of that series would be the $(p - 1)$th, and the next the $(p - 2)$th, and so on.

Diagrams of Fabry and Perot's original apparatus[1] are shown in Figs. 8 and 9 in side and end elevation respectively. It is absolutely necessary in such an interferometer that the silvered glass surfaces be always kept absolutely parallel to one another; very delicate adjustments must therefore be provided to correct for the errors in parallelism produced when the thickness of the air layer is altered. In the present apparatus there are the following adjustments: first, for altering the distance between the silvered surfaces there is a rapid adjustment, a fine adjustment which allows one to count the fringes, and finally a very delicate adjustment, which is limited to a few thousandths of a millimetre; secondly, the orientation adjustments are of two kinds, one a rapid and coarse adjustment, and the other a very fine and slow adjustment. The fine adjustments in each case are obtained by the pressure of a small rubber bag full of water against steel plates; this method is capable of giving extraordinarily small movements.

L and L′ (Fig. 8) are the two supports for the silvered glass plates; each of the latter is 40 mm. in diameter. One face of each is perfectly plane, one being silvered, while the other is very nearly plane. The two faces of each disc are not parallel to one another, but enclose an angle of about 1′, so as to evade any possibility of interference being set up by the glass discs themselves.

L, which is next to the observer, can be subjected to very rapid orientation movements and very small and delicate adjustments parallel to the path of the light. The first of these motions is obtained by rotation round two axes, O and O′ (Fig. 9), which are vertical and

[1] *Ann. Chim. et Phys.*, **22**, 564 (1901).

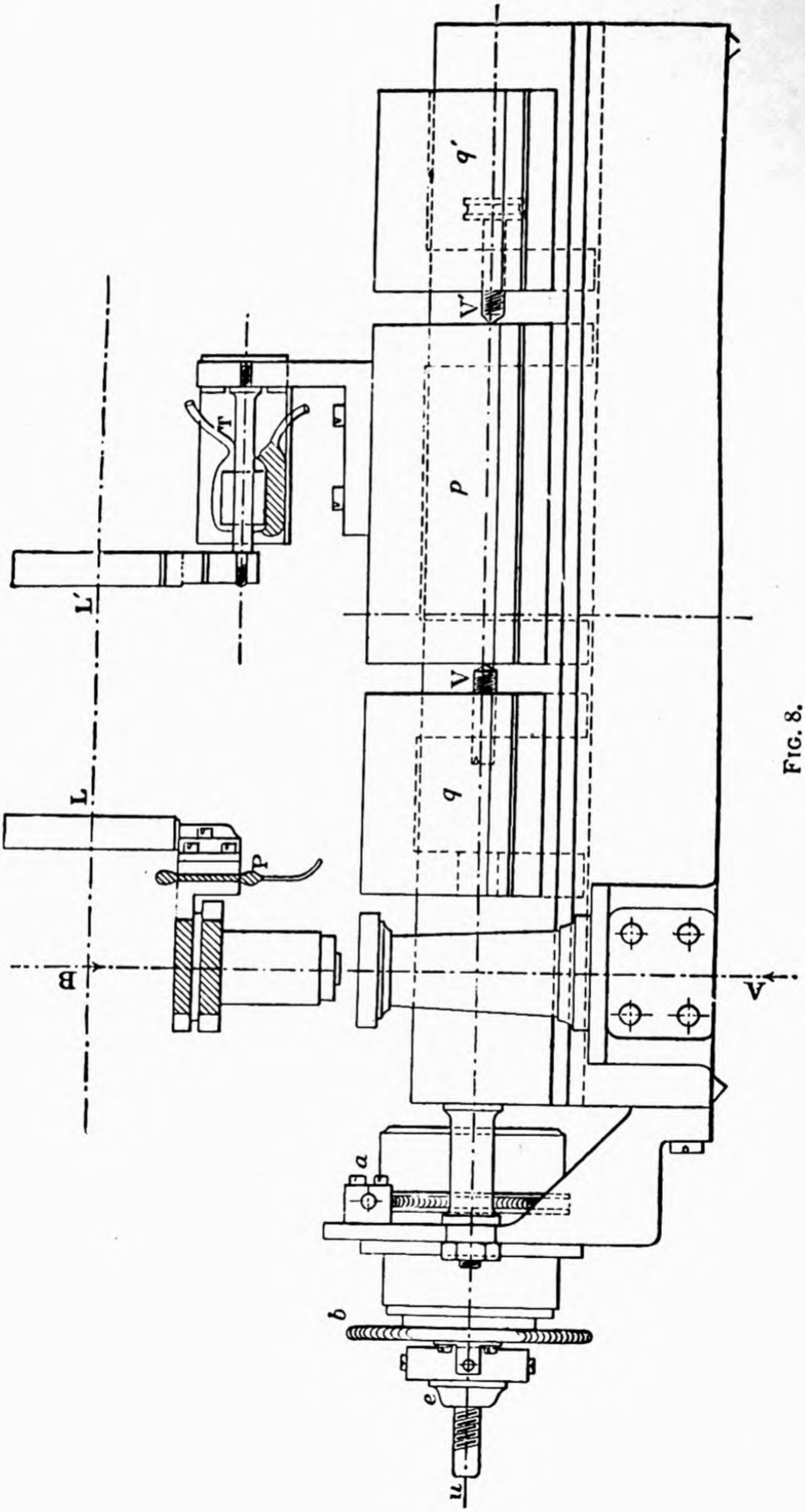


FIG. 8.

horizontal respectively. The fine parallel adjustment is obtained by the deformation of a strong steel spring, P, the centre of which is fixed on one side to the axis O, and on the other to the carrier L. This spring is formed of two steel strips, 16 × 2 × 0·4 cm., which are joined together at the ends; stopping pieces are placed between the strips at the ends E and E′, to keep them a short distance apart. A small caoutchouc bag full of water is put between the centres of the strips; this bag is connected by a tube to a movable reservoir of water. An alteration of 1 cm. in the height of this reservoir produces a displacement of the disc of 0·15 μ.

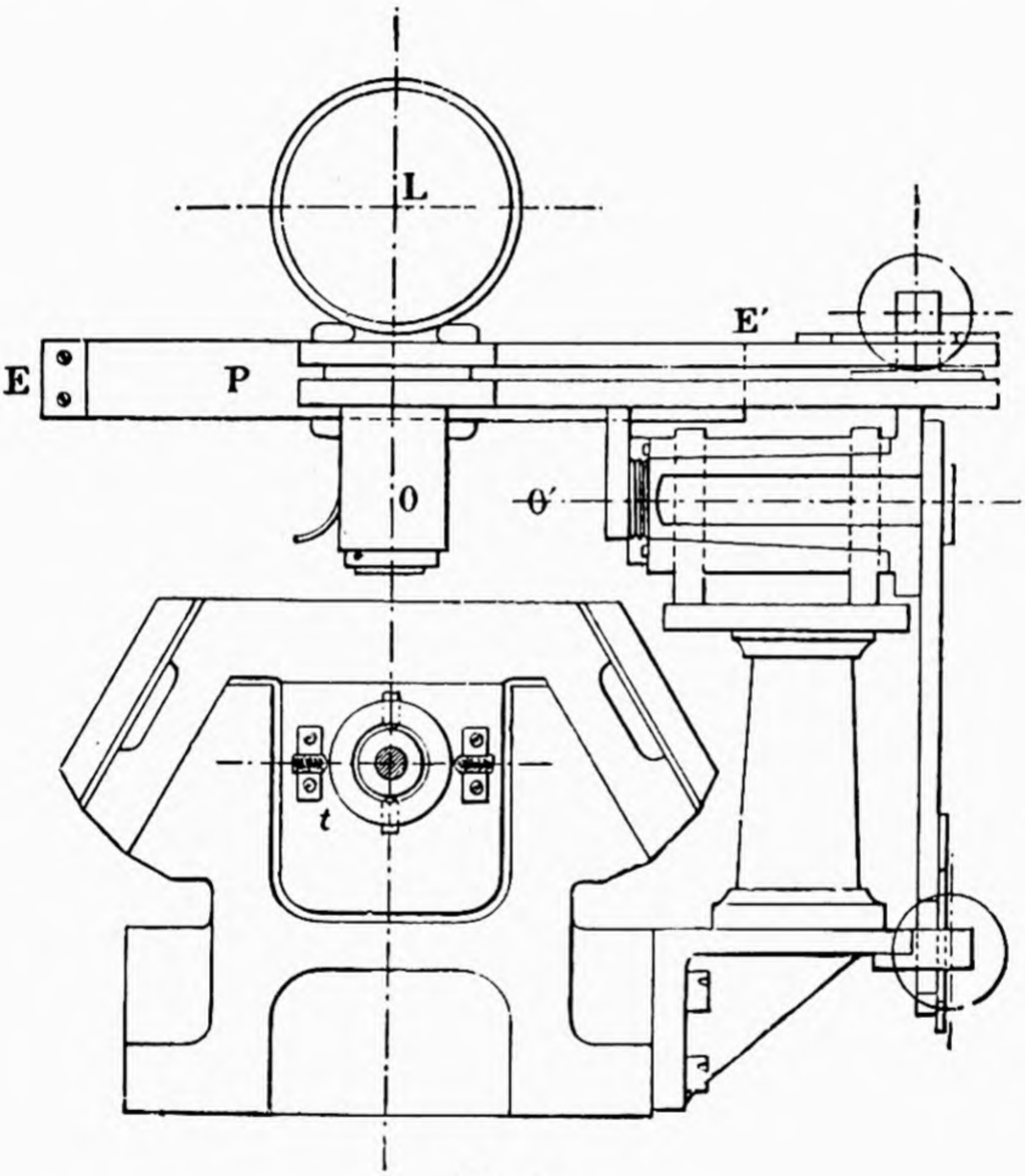


FIG. 9.

The carrier L′ can be subjected to small orientation displacements and large movements parallel to the path of the light. L′ is fixed at the end of the steel pillar T, on which is screwed a cube of bronze; two rubber bags, one underneath and the other at the side, serve to give very small horizontal and vertical displacements to L′. A change of 1 cm. in the height of the attendant water reservoirs produces an angular displacement of 0·25″. The parallel movement is obtained as follows: the bracket carrying L′ is fixed to p, which is a bronze block, working extremely smoothly and truly upon V-shaped slides.

The block p sits between two smaller blocks, q, q', and as these two blocks move one way or the other, they push the block p by means of the pointed thrust pieces V, V'. In this method of moving p it can be seen that p is entirely free upon its slides, and rests thereon by its own weight, the only force applied to it being truly parallel to its movements. There is thus no chance of any rocking motion, such as would certainly be produced were p moved directly by the micrometer screw. Fabry and Perot found it possible in this way to follow the fringes while moving p, which would otherwise have been impossible. The two blocks q and q' are both rigidly fastened to the micrometer screw, which can be seen projecting from the apparatus at u; this screw is moved backwards or forwards by the rotation of the nuts a or b, a having a tangent-screw arrangement for slow motion.

In order to gain some idea of the distance between the silvered

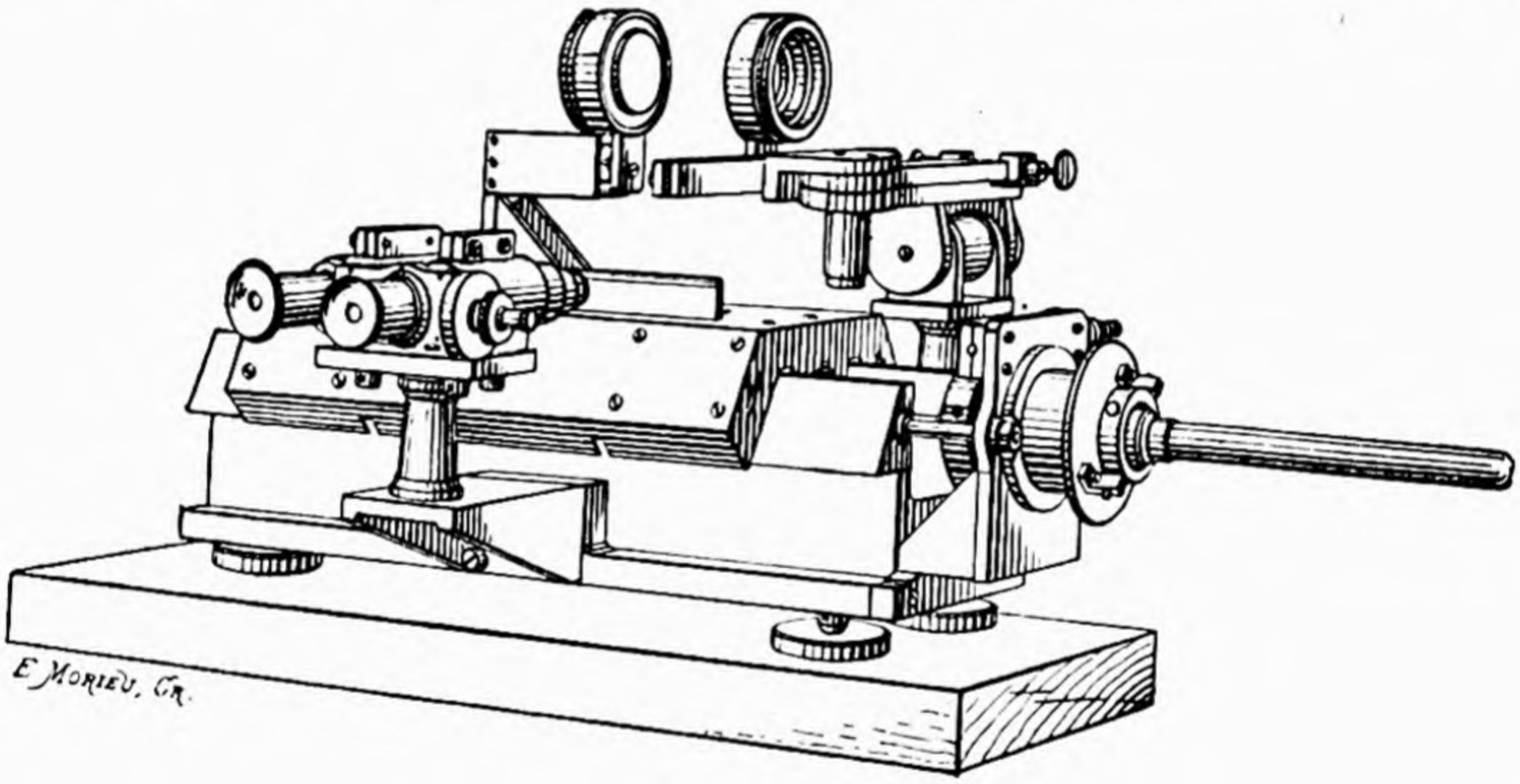


FIG. 10.

surfaces at any time, a micrometer scale is fitted to the instrument, upon which the position of p can be read at any instant by means of a microscope with a micrometer eyepiece. This scale is graduated in $\frac{1}{5}$th mm., and the zero is determined upon it by direct observation, such as the first complete disagreement of the two mercury yellow rays. The instrument is shown in its complete form in Fig. 10.

One of the first applications of this interferometer by Fabry and Perot was to the study of the structure of certain spectrum lines by the examination of the fringes they produce. It is necessary for this purpose that the apparatus be only illuminated with the rays it is required to examine; if these rays form part of a very simple spectrum it may be sufficient to cut off the other rays by means of absorbing solutions, but the best method is to analyse the light by passage through one or two carbon bisulphide prisms, and to focus the required rays upon a slit by means of a lens. A second lens receives the rays

coming through the slit, and directs them as a converging beam upon the silvered surfaces. At first the air layer is made as small as possible, and then it is slowly widened until the fringes double themselves, and the first condition of disagreement is reached. As was pointed out before, the nearer a fringe ring is to the axis of the beam of light, *i.e.* the smaller the radius of a fringe, the greater the corresponding difference of path.

The following rays were examined, the various substances being excited in tubes similar to those used by Michelson and by Hamy [1]—

Thallium : $\lambda = 5351$ A.U.

This ray doubles itself very easily, the first effect showing itself when the thickness of the layer ($= e$) is equal to 1·5 mm. ; a weaker ring is then to be seen just inside each bright ring, showing that the weaker component has the larger wave-length. The condition of complete disagreement is obtained when $e = 6{\cdot}35$ mm.

From these numbers the number of the order $\left(= \frac{12{\cdot}7}{0{\cdot}0005351}\right)$ is found to be nearly 23,800, whence $\frac{\epsilon}{\lambda} = 21 \times 10^{-6}$.

On still further increasing e it is found that the principal component itself is double, being composed of a brighter and weaker component, the weaker component having the greater wave-length ; for this pair $\frac{\epsilon}{\lambda}$ was found to be 3×10^{-6}. It follows that the green thallium radiation is triple, being composed of one strong and two weaker components. The last two are apparently of the same intensity, and are both on the red side of the principal component, the values of $\frac{\epsilon}{\lambda}$ being respectively 3×10^{-6} and 21×10^{-6}.

The cadmium radiations were examined, and it was found that the red ray is quite simple, as was shown originally by Michelson.

The results obtained by Fabry and Perot differ to a certain extent from those obtained by Michelson by his method of plotting the visibility curves. The reason of this lies in the fact that in the case of a given visibility curve, especially if complex, many hypotheses may be chosen which give on calculation a curve of similar form to that observed. For example, one cannot be certain in the case of a double source of two lines of unequal brightness as to how these are situated with regard to one another. It is important to notice that, if the values obtained from the above measurements be substituted in Michelson's expression for visibility, the visibility curves obtained agree with those actually observed by him ; these results are, therefore, really in perfect accord with those of Michelson.

The next application by Fabry and Perot of their interferometer was in the direction of the comparison of wave-lengths among

[1] See p. 97.

themselves and the measurement of length in terms of wave-lengths.[1] According to the equation $p = \frac{\Delta}{\lambda}$, as has already been said, when p is a whole number a bright fringe is produced, of which p is the number of the order; when p is not a whole number, the fractional part represents the difference of phase between the two first interfering waves, and therefore p should be defined as the order of interference corresponding to a difference of path Δ. Let us imagine that the incident light consists of two vibrations, red and green, of wave-lengths λ and λ' ($\lambda > \lambda'$). The two systems of fringes then seen can easily be distinguished by their difference of colour. When we pass from one red fringe to the next, the difference of path increases by λ, and similarly from one green fringe to the next, by λ'; as λ' is smaller than λ, the green fringes are closer together than the red. It is possible then to find a region where two green fringes are placed between two red fringes; this is an approximate coincidence of the two systems.

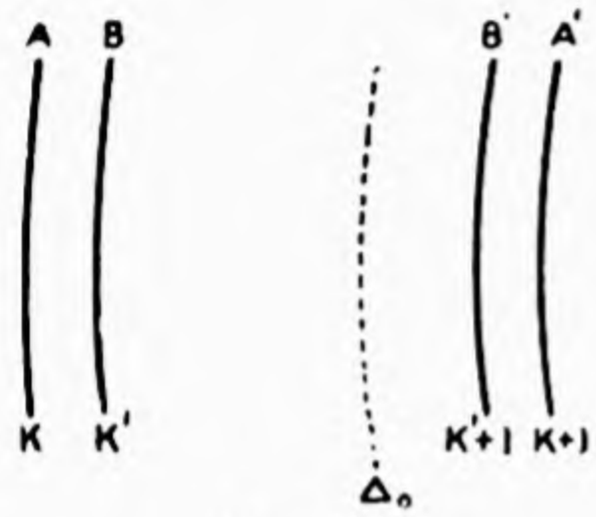


FIG. 11.

In Fig. 11 A and A′ are two consecutive red fringes, B and B′ two consecutive green fringes. Let K and K + 1 be the order numbers of A and A′, and K′ and K′ + 1 the orders of B and B′, and let $K' - K = m$.

Now, at each point in the field of view there is a definite value of Δ, and therefore a definite value of the order of interference, $p = \frac{\Delta}{\lambda}$ for the red, and $p' = \frac{\Delta}{\lambda'}$ for the green rays.

Along the curve B, p' is a whole number and equal to K′, whilst p, which is equal to K along A, is a little larger than K; along B, therefore, we have—

$$p' - p < m.$$

Similar reasoning shows that along B′—

$$p' - p > m.$$

It follows that $p' - p$ increases with Δ, and that there must be a particular value, Δ_0, for which—

$$p' - p = m.$$

This value of the difference of path, called by Fabry and Perot the difference of path at coincidence, occurs when the difference $p' - p$ between the orders of interference is a whole number, m. It corresponds to an ideal line in the field of view, and is defined by the equation—

$$\frac{\Delta_0}{\lambda'} - \frac{\Delta_0}{\lambda} = m.$$

It follows that

$$\Delta_0 = m\frac{\lambda\lambda'}{\lambda - \lambda'}.$$

[1] *Ann. Chim. et Phys.*, **16**, 289 (1899).

The phenomenon is thus periodic, for the differences of path at coincidence are multiples of a length which may be called the period—

$$P = \frac{\lambda\lambda'}{\lambda - \lambda'}.$$

One can express this period in terms of the wave-length of any ray, *e.g.* in terms of λ—

$$\omega = \frac{P}{\lambda} = \frac{\lambda'}{\lambda - \lambda'},$$

and similarly in terms of λ'—

$$\omega' = \frac{P}{\lambda'} = \frac{\lambda}{\lambda - \lambda'}.$$

Evidently $\omega' = \omega + 1$, because at the first coincidence n waves of length λ are equal to $n + 1$ waves of length λ'.

The mth coincidence takes place when $\Delta = mP$, and the order of interference of waves λ is $m\omega$, and of waves λ', $m\omega'$, which $= m\omega + m$.

If $m\omega$ happens to be a whole number K, then the coincidence will be exact, and the appearance will be as in Fig. 12.

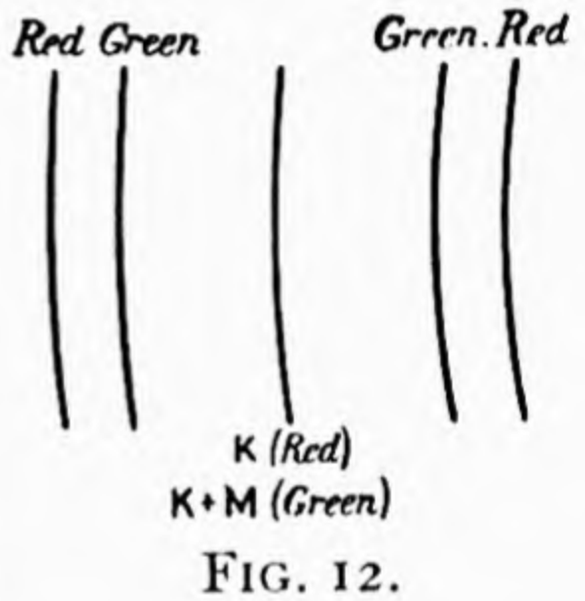


FIG. 12.

Generally, we put $m\omega = K + \theta$, K being a whole number and θ lying between 0 and 1. When θ is $= 0$ or 1, then the coincidence is exact, as in Fig. 12; and when θ has some intermediate value, the coincidence is inexact, as in Fig. 11. If a and a' are the distances AB, B'A' in Fig. 11 (strictly speaking the differences in path denoted by the distances AB and B'A'), then—

$$\theta = \frac{a}{a + a}.$$

It is possible when λ and λ' are not too close to measure θ from the observation on a coincidence.

Clearly from the above P is inversely proportional to the difference between λ and λ'; if P corresponds to four or five fringes one can observe the coincidences with accuracy. When P is about fifteen fringes, observations of θ are more difficult; but when P is very large, as with the D rays of sodium, it is better to observe the regions of complete disagreement of the fringes, for in this case the observations are impossible on the coincidences, as the fringes belonging to the two systems are so alike in colour and are so confused with one another. The condition of complete disagreement is, however, easily estimated, and then, of course, we have—

$$\Delta = (m + \tfrac{1}{2})P.$$

In their work Fabry and Perot used as standards the values for the wave-lengths of the three cadmium lines measured by Michelson

and Benoit. They found that the blue line is not sufficiently simple in its structure for use with any but small differences of path, and they selected the cadmium green line as their final standard of reference.

The following description may be given of the determination of the wave-lengths of the two yellow lines and the green line of mercury by means of the interferometer, this method of measurement being typical of those carried out by Fabry and Perot with this apparatus :—

The rays from both the sources, mercury and cadmium, are simultaneously thrown into the apparatus, and it is absolutely indispensable that the two beams of light should be exactly superposed. The method used is shown in Fig. 13, where T and T′ are the two sources, and A a half-silvered mirror. E and E′ are two movable screens, used when only one source is required. Absorbents may also be used to cut off

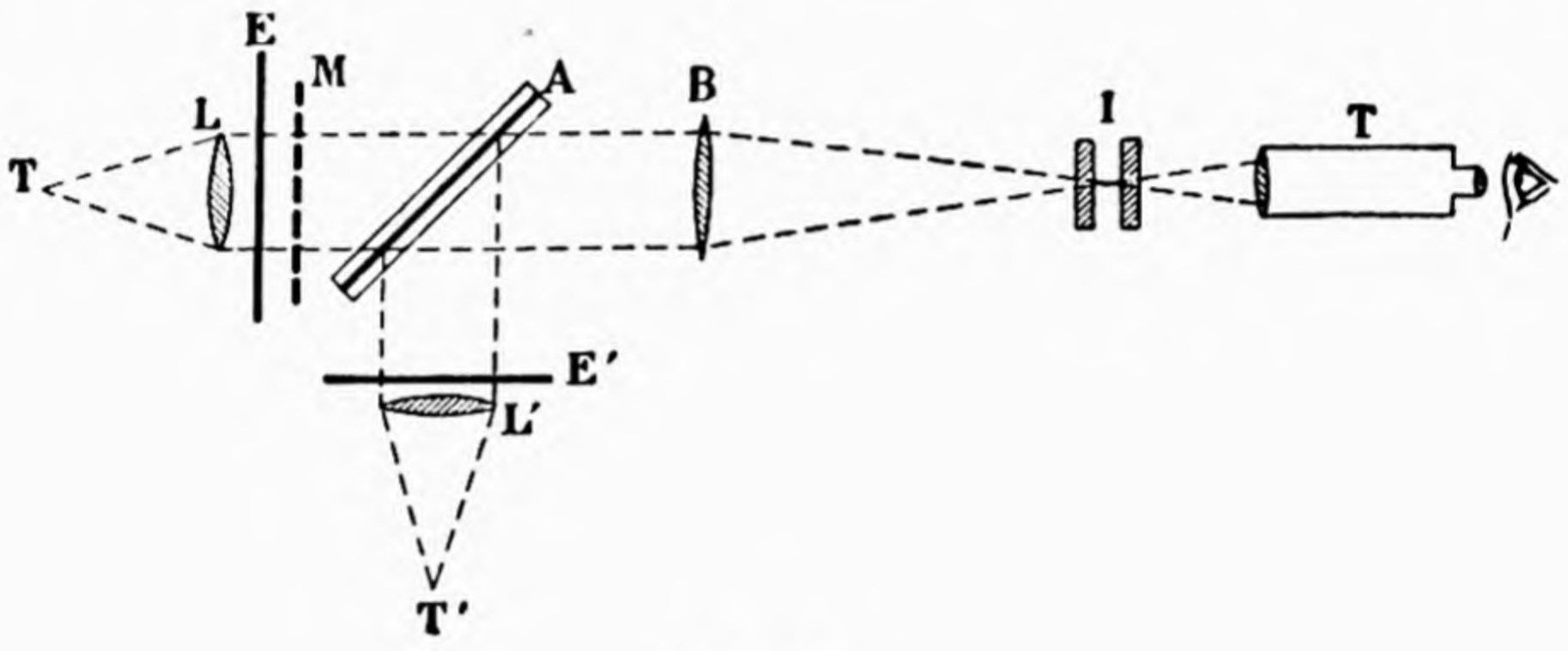


FIG. 13.

the rays from either source. The interferometer is placed at I; the rest of the apparatus explains itself.

It is necessary in making these measurements that the wave-lengths of the rays to be dealt with be approximately known; these may, of course, be readily found with a grating, and the values used in this investigation were—

$$\lambda_{Y_1} = 5790{\cdot}49 = Y_1$$
$$\lambda_{Y_2} = 5769{\cdot}45 = Y_2$$
$$\lambda_{G_m} = 5460{\cdot}97 = G_m.$$

All the measurements made were referred to the green ray of cadmium (called G).

From the above values of the wave-lengths of the mercury rays, one approximate value of the period of coincidence in terms of the ray G was calculated for the two yellow rays of mercury (Y_1 and Y_2). This is given by the expression $\frac{5790{\cdot}49 \times 5769{\cdot}45}{21{\cdot}04 \times 5085{\cdot}824}$, and is equal to 312·2.

Similarly, the period of the rays G_m and cadmium red (R) were found in terms of the ray G to be 14·5569 and 4·759901 respectively.

It is convenient to have the scale of the interferometer calibrated in terms of the coincidences of two rays. The two yellow rays of mercury are very suitable for this purpose; the apparatus is illuminated by these rays alone, and the two silver surfaces are brought as near together as possible. They are then slowly widened until the first coincidence is observed; the reading on the scale is taken, and the plates again separated until the second coincidence is seen, when the scale is again read, and so on. In this way a calibration of the scale is obtained from which at any time when a coincidence is observed the number of it can at once be obtained.

The first series of observations was made as follows:—

1. The silvered plates were so set as to observe, near the centre of the field, a complete disagreement between the fringes of the rays Y_1 and Y_2, and on reference to the scale and the table it was found that this disagreement occurred between the sixth and seventh coincidences.

2. The mercury rays were then removed and the cadmium rays R and G thrown in without altering the interferometer in any way; it was found that an exact coincidence occurred in the same part of the field as did the complete disagreement in the first observation; that is to say, the nth red fringe exactly coincided with the pth green fringe.

3. On comparing the rays G and G_m it was found that the $(p - 5)$th fringe of the former was in complete disagreement with two fringes of the ray G_m.

4. On comparing the rays R, Y_1, and Y_2, it was found that the $(n - 2)$th fringe of the first was in complete disagreement with two fringes, one due to Y_1 and the other due to Y_2, the fringe due to Y_2 being on the inside. The $(n - 2)$th fringe of G therefore exactly coincided with a hypothetical ray of mean wave-length between Y_1 and Y_2.

5. The $(n + 2)$th red fringe was in complete disagreement with a blue and a green cadmium fringe.

Now, from the approximate wave-lengths of Y_1 and Y_2 above given, it follows that the sixth disagreement takes place at the 2028th green cadmium fringe. The period is equal to 312, and therefore the disagreement dealt with occurred at the $\left(312 \times 6 + \frac{312}{2}\right)$th fringe.

Therefore p is about 2028, and n about $2028 \times \frac{\lambda_G}{\lambda_R} = 1602$.

In the following table are given the numbers of the red cadmium fringes which coincide with green cadmium fringes, and also the disagreements between green and blue fringes of cadmium expressed in terms of the red ray of cadmium, both calculated from Michelson's measurements—

Coincidences. Red and green cadmium.	Disagreements. Green and blue cadmium.
1597·8	1584·7
1601·5	1598·0
1605·3	1611·2
1609·0	1624·5
1612·8	1637·7
1616·5	

Now, it was stated that the nth red and pth green were in *exact* coincidence; therefore n must be a whole number, about 1602. Evidently 1609 is the only possible value; further, from (5) the $(n + 2)$th red fringe is situated at a disagreement between a green and a blue cadmium fringe, and this is shown by the 1611·2 in the second column. The corresponding value of p is, therefore, 2037.

Again, from (3) the 2032nd fringe of G was in complete disagreement with two fringes of the ray G_m. The following table gives the numbers of the fringes of the ray G in such disagreement, calculated from the period given above (14·5569) :—

	Number of disagreement.
2015·5	138
2030·0	139
2044·5	140

The 139th disagreement was evidently observed, and as the calculation gives the 2030th fringe, whilst the observation gives the 2032nd, it follows that the period obtained above from the wave-lengths is wrong. A better value is—

$$\omega = \frac{2032}{139{\cdot}5} = 14{\cdot}5663.$$

Again, from (4) the 1607th red cadmium fringe is in exact coincidence with the mean of the two mercury yellow rays. The calculation from the period obtained from the above wave-lengths shows that the 183rd coincidence takes place at the fringe 1605·8; evidently here also the period must be slightly corrected.

From these first series of measurements we thus obtain more accurate values of the period of coincidence of the rays the wave-lengths of which are to be determined, and from these the tables of coincidences may be more accurately calculated. It becomes possible then to work with thicker interference layers, when still more accurate measurements may be made. From these new values the periods are again obtained with still greater accuracy, and so on. Fabry and Perot reached layers in these measurements of 32 mm., which correspond to the 125,000th fringe of the green cadmium ray.

The final values obtained were—

$$\lambda = 5460{\cdot}7424$$
$$\lambda = 5790{\cdot}6593$$
$$\lambda = 5769{\cdot}5984$$

The probable error in the green ray is given by $\frac{\delta\lambda}{\lambda} = \pm 10^{-7}$, or about $\frac{1}{10000000}$; in the case of the yellow rays it is somewhat greater.

This beautiful apparatus leaves very little to be desired as an interference apparatus for examination of the structure of radiations and the determination of absolute wave-length. It has further a great advantage over an ordinary apparatus in that absorption lines such as the Fraunhofer lines can be examined. The measurement of wave-length, it is true, is a very tedious process, and hence Fabry and Perot,[1] profiting by their experience with their interferometer, have adopted fixed air layers as interference apparatus, the widths of which

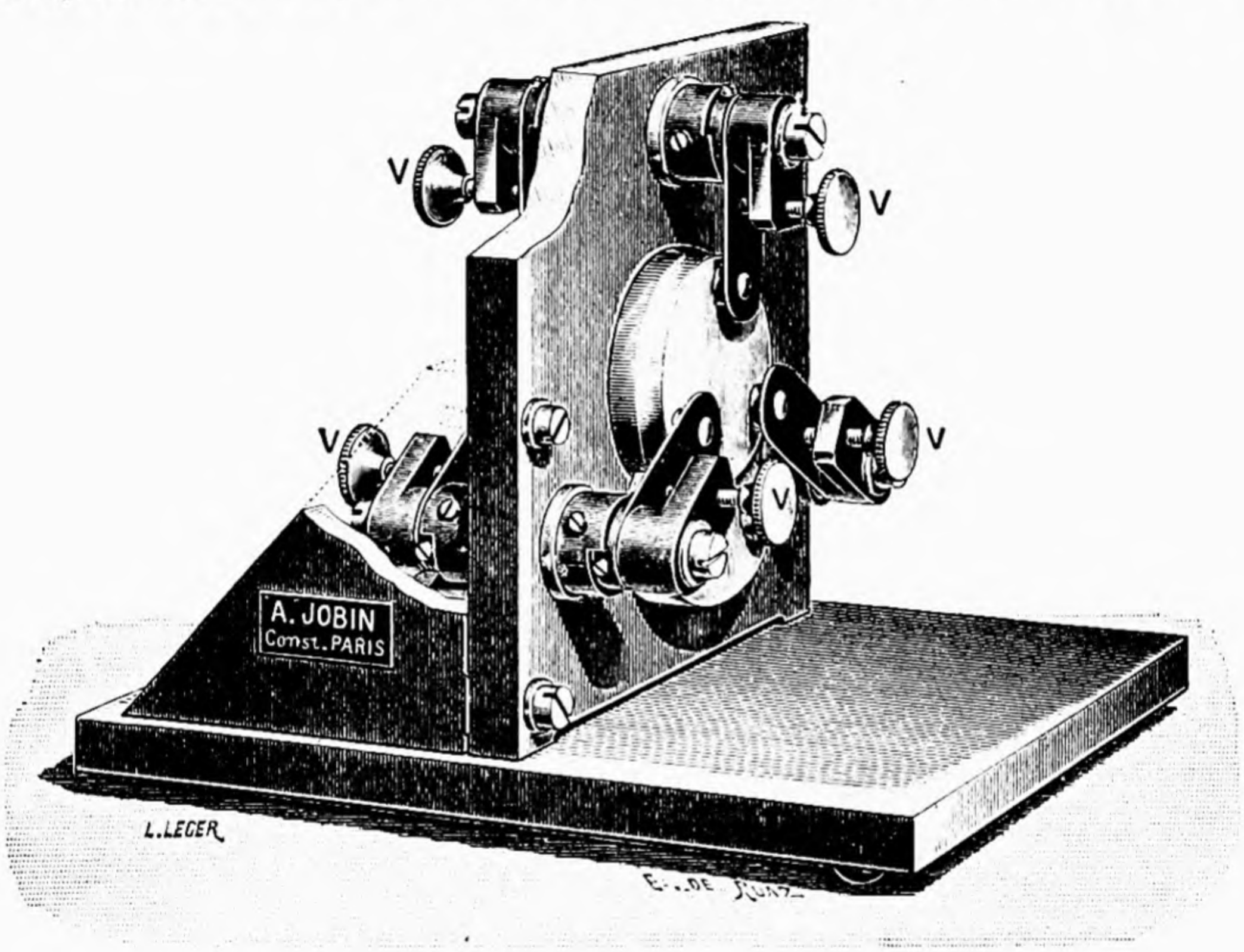


FIG. 14.

are determined once and for all. They called these apparatus standards (*étalons*), and made use of three, which were 2·5 mm., 5 mm., and 10 mm. in thickness, respectively. With these they measured the wave-lengths of certain rays in the emission spectrum of the iron arc, and also in the solar spectrum.

These étalons consist of two half-silvered glass plates, as before, which are kept apart by polished steel supports. The plates are kept pressed against the supports by binding screws, by means of which they are very carefully adjusted and made parallel. The apparatus is shown in Fig. 14.

The method of using these étalons is as follows: The order of

[1] *Ann. Chim. et Phys.*, **25**, 98 (1902).

interference at the centre of a system of rings is determined successively for the two radiations to be compared; this can be done first for one and then for the other, because the thickness of the interfering layer will not change during a measurement. Let one of these, with wave-length λ, be as usual the green ray of cadmium, and let P be the number of the order of one of the fringe rings obtained with it, and let this be the first ring, counting from the centre. The order of interference at the centre will be $p = P + \alpha$; P is readily found from the knowledge of the thickness of the air layer, supposed previously determined. It only remains to determine the fraction α, which lies usually between 0 and 1.

The diameter of the fringe is evidently proportional to α, and it is therefore possible to determine α from a measurement of the diameter of the ring P.

As shown previously, the order of interference at the centre is—

$$p = \frac{2e}{\lambda}, \text{ if } e \text{ is the thickness of the air layer.}$$

In a direction making an angle i with the normal it is $\frac{2e}{\lambda}\cos i$, or $p \cos i$. If x is the angular diameter of the ring P, then, the telescope being focussed for parallel rays,

$$p \cos \frac{x}{2} = P,$$

and as x is very small, $$p = P\left(1 + \frac{x^2}{8}\right);$$

thence
$$\alpha = p - P$$
$$= P\frac{x^2}{8}.$$

Similarly, with a radiation of wave-length λ' we have—

$$\alpha' = P'\frac{x'^2}{8}.$$

Now, since the thickness of the layer is constant—

$$\lambda(P + \alpha) = \lambda'(P' + \alpha'),$$

therefore
$$\lambda' = \lambda\frac{P + \alpha}{P' + \alpha'};$$

and by substitution of the values for α and α' above found we have—

$$\lambda' = \lambda\frac{P}{P'}\left(1 + \frac{x^2}{8} - \frac{x'^2}{8}\right).$$

From this $\frac{\lambda'}{\lambda}$ can be determined by observation.

It is first of all necessary to determine the thickness of the standards to be employed in the investigations. This is done by the method of superposed interfering layers; that is to say, a beam of light is sent through two layers in series, the most satisfactory arrangement being that shown in Fig. 15.[1]

It can readily be shown that if the two thicknesses be the same, a beam of white light will give a white fringe along the points corresponding to equal thicknesses. This also occurs when the thicknesses of the layers are in simple proportion. As a result of this it is possible to determine accurately the thickness of the air layer in a given étalon, by comparison with the interferometer or a graduated étalon. The graduated étalon is made with the glass plates set at a very small angle to one another. There is a scale ruled on one of the inner glass surfaces, and the thickness of the layer is known from previous measurements at any point on the scale. For the actual method employed, the original memoir must be consulted. It must be imagined that the thicknesses of all the étalons used are known in terms of the standard ray (cadmium green, principal component).

Now, changes are readily produced in the thickness of the layer by

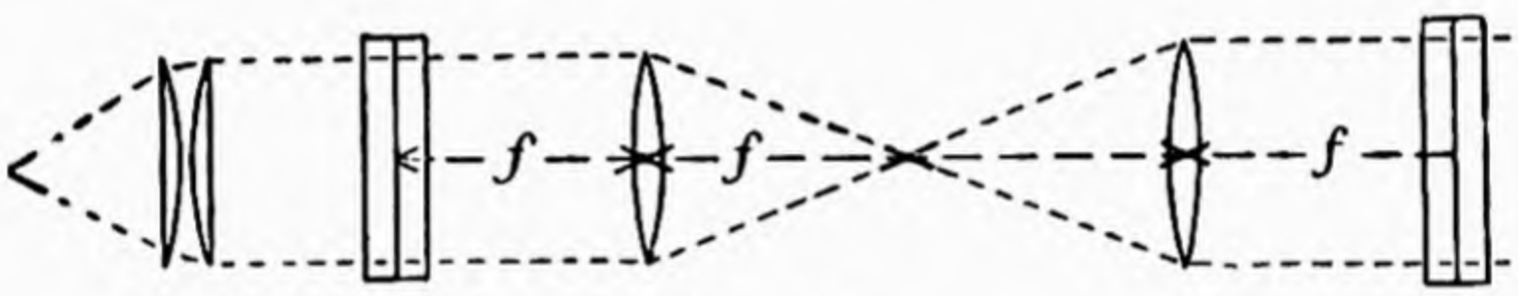


FIG. 15.

alteration of temperature, and therefore in practice only a small area of the layer is used, and the cadmium green fringes are observed and measured immediately before and after a measurement of the new ray.[2] Since the thicknesses are known, the number of the order of the first ring can always be found at once; in the case of the cadmium green from the standardisation, and in the case of a new ray from its approximate wave-length, supposed already known.

The measurement of the diameter of the ring is carried out by means of a micrometer eyepiece in the telescope, the readings of this instrument having been already calibrated in some convenient way.

A small correction has to be introduced in the measurements due to the change of phase at reflection. In the expression—

$$e = p\frac{\lambda}{2},$$

in which p is the order of interference at the centre, e, it must be remembered, is the optical thickness of the air layer; it is not necessarily the distance between the two silver surfaces. Hitherto we have

[1] *Ann. Chim. et Phys.*, **12**, 459 (1897).

[2] The actual expansion of a 10 mm. étalon was about 0·0001 mm., *i.e.* about four fringes for 10°.

reasoned as if e did not vary with λ, but in actual practice this is not strictly true, on account of the fact that the change of phase at reflection varies very slightly with the wave-length. In other words, e varies slightly with λ, so that if e be determined for a standard ray, λ, it must not be assumed that e is the same for another ray, λ', if $\lambda - \lambda'$ is large. Let us consider two rays, λ and λ', therefore, for which the optical thicknesses of the air layer are e_λ and e_λ', and are slightly different; then, if p and p' be the orders of interference—

$$2e_\lambda = p\lambda \text{ and } 2e_\lambda' = p'\lambda',$$

whence

$$\lambda' = \frac{e_\lambda' p}{e_\lambda p'}\lambda.$$

Hitherto we have assumed $\lambda'_0 = \frac{p}{p'}\lambda$.

To the ordinarily found value λ'_0 we must, therefore, add a small correction—

$$\gamma = \lambda' - \lambda'_0 = \frac{p\lambda}{p'} \cdot \frac{e_\lambda' - e_\lambda}{e_\lambda} = 2\frac{e_\lambda' - e_\lambda}{p'} \quad . \quad . \quad . \quad (1)$$

This correction is readily found by observations upon two rays the wave-lengths of which are absolutely known. The two silvered plates are dismantled from the standard, and mounted upon the interferometer, and brought almost into contact. The apparatus is then illuminated by the two rays, for example, the red and green of cadmium, which we may denote by λ and λ'. The two plates are then slowly separated until an exact coincidence is found; if this be the qth coincidence, then the pth fringe of the ray λ is in exact coincidence with the $(p + q)$th fringe of λ', and thus—

$$2e_\lambda = p\lambda \text{ and } 2e'_\lambda = (p + q)\lambda',$$

therefore

$$e_\lambda' - e_\lambda = \frac{(p + q)\lambda'}{2} - \frac{p\lambda}{2}$$

$$= \frac{q\lambda'}{2} - \frac{p(\lambda - \lambda')}{2}$$

$$= \frac{\lambda - \lambda'}{2}\left(q\frac{\lambda'}{\lambda - \lambda'} - p\right)$$

$$= \frac{\lambda - \lambda'}{2}\rho,$$

where

$$\rho = \frac{q\lambda'}{\lambda - \lambda'} - p.$$

It will be seen that $\frac{\lambda'}{\lambda - \lambda'}$ is the period of coincidence in terms of λ. The following are the results obtained with one of the étalons by Fabry and Perot :—

(*a*) Two cadmium rays, $\lambda = 6438$ and $\lambda' = 5085$.

$$\rho = 0{\cdot}065,$$

therefore $$e_\lambda - e_\lambda' = -\ 4{\cdot}4\mu\mu.$$

(*b*) Cadmium red and mercury green rays, $\lambda = 6438$ and $\lambda' = 5461$.

$$\rho = 0{\cdot}042,$$

therefore $$e_\lambda - e_\lambda' = -\ 2{\cdot}1\mu\mu.$$

(*c*) Mercury green and blue rays, $\lambda = 5461$ and $\lambda' = 4358$.

$$\rho = 0{\cdot}12,$$

therefore $$e_\lambda - e_\lambda' = +\ 6{\cdot}6\mu\mu.$$

These are then all reduced to the standard of the cadmium green, and the values of the correction γ obtained from equation (1). These values are then put upon a curve; they vary from $-$ 0·003 A.U. at $\lambda = 6500$ to $+$ 0·002 A.U. at $\lambda = 4500$.

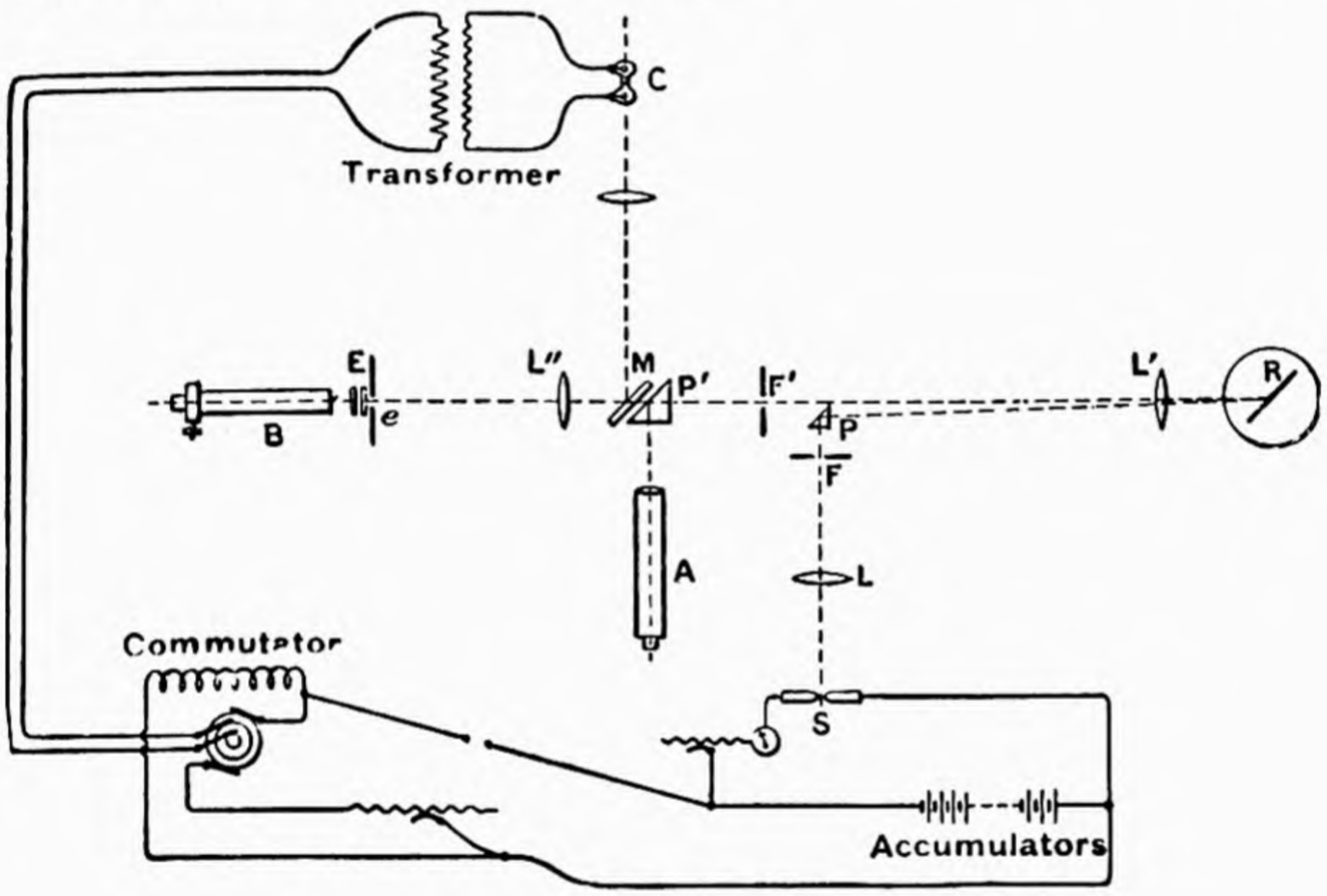


FIG. 16.

By means of three étalons Fabry and Perot measured the wave-lengths of fourteen lines in the arc spectrum of iron, and thirty-three in the solar spectrum. In both series of measurements the apparatus was so arranged that either the cadmium green ray or the required ray in the iron or solar spectrum could be thrown upon the interference étalon; in the case of the iron spectrum, the arrangement used is shown in Fig. 16.

S was the iron arc, an image of which was focussed in the slit F by the lens L; the rays coming through the slit passed through the totally reflecting prism P, and thence through the lens L′ on to the plane grating R; the diffracted rays passed back, and were focussed by the lens L′ on to the slit F′. By rotating the grating R any required line could be brought on to the slit F′. The rays coming through F′ passed straight on through the half-silvered parallel plate M, and were

directed as a converging beam on to the interference standard E by the lens L″. The prism P′ could, if desired, be raised and brought into the path of the rays in order to examine the spectrum at the telescope A. The cadmium tube was at C, and the rays therefrom

TABLE I.

Element.	Wave-length in tenth metres.	Source.
Mercury	5790·6593	Arc *in vacuo*.
	5769·5984	,, ,,
	5460·7424	,, ,,
	4358·343	,, ,,
Zinc	6362·345	"Vibrator" *in vacuo*.[1]
	4810·535	,, ,,
	4722·164	,, ,,
	4680·138	,, ,,
Copper	5782·159	"Vibrator" *in vacuo*.
	5782·090	,, ,,
	5218·202	,, ,,
	5153·251	,, ,,
	5105·543	,, ,,
Silver	5465·489	"Vibrator" *in vacuo*.
	5209·081	,, ,,
Sodium	5895·932	Flame spectrum.
	5889·965	,, ,,
Lithium	6707·846	Flame spectrum.
Iron	6494·992	Arc.
	6230·733	,,
	6065·489	,,
	5763·323	,,
	5615·657	,,
	5586·775	,,
	5506·783	,,
	5434·525	,,
	5302·321	,,
	5232·954	,,
	5083·345	,,
	5001·887	,,
	4859·763	,,
	4736·785	,,

[1] For a description of this apparatus. see p. 94.

were reflected at M, and thence passed into the apparatus. Screens were employed to cut off either one or the other beam of light; *e* was a fixed screen pierced with a small hole of 3 mm. diameter, to localise the region of the étalon E which was employed. The apparatus used for the solar spectrum was somewhat similar, with this difference, that a concave grating was employed in place of the plane one. In the case of iron, only a few lines could be measured with a very great degree of accuracy, because they are not, as a rule, of sufficient fineness.

For a description of the actual experimental details, the original memoir must be consulted.

In Table I. is given the first list of wave-lengths[1] determined by Fabry and Perot, both with the interferometer and with the interference étalons as last described

In Table II. are given the wave-lengths of the lines in the solar spectrum, which were also determined.

TABLE II.

Fabry and Perot. λ.	Rowland. λ_R.	$\frac{\lambda_R}{\lambda}$.
6471·666	6471·885	1·0000338
6408·027	6408·233	1·0000321
6322·700	6322·907	1·0000327
6230·746	6230·943	1·0000316
6151·639	6151·834	1·0000317
6065·506	6065·709	1·0000335
6016·650	6016·861	1·0000351
5987·081	5987·290	1·0000349
5934·666	5934·881	1·0000362
5862·368	5862·582	1·0000365
5763·004	5763·218	1·0000371
5715·095	5715·308	1·0000373
5586·778	5586·991	1·0000381
5506·794	5507·000	1·0000374
5497·536	5497·735	1·0000362
5434·544	5434·740	1·0000361
5409·800	5410·000	1·0000370
5367·485	5367·669	1·0000343
5345·820	5345·991	1·0000320
5339·956	5340·121	1·0000309
5247·587	5247·737	1·0000286
5247·063	5247·229	1·0000316
5171·622	5171·778	1·0000302
5123·739	5123·899	1·0000312
5090·787	5090·954	1·0000328
5001·881	5002·044	1·0000326
4923·943	4924·107	1·0000333
4859·758	4859·928	1·0000350
4783·449	4783·613	1·0000340
4736·800	4736·963	1·0000344
4704·960	4705·131	1·0000363
4643·483	4643·645	1·0000349

[1] *Comptes Rendus*, **130**, 492 (1900), and *Ann. Chim. et Phys.*, **25**, 98 (1902).

The last column in the table of solar wave-lengths expresses the ratio of Rowland's measurements to those given, and in Fig. 17 these ratios are plotted against the wave-lengths, the ratios being taken as the ordinates, and the wave-lengths as the abscissæ.

The curve should be, of course, a horizontal straight line, but as the differences from a mean straight horizontal line are enormously greater than the errors of experiment, this curve established the fact that there is a periodic error in Rowland's system of standard wave-lengths.

I have given this full account of Fabry and Perot's work because it was the first determination of wave-lengths made by interference methods and based upon Michelson and Benoit's standards. Furthermore, a knowledge of the methods employed by them is necessary to understand the modern methods which are based entirely on the Fabry and Perot procedure.

The discrepancy between the new measurements and the Rowland

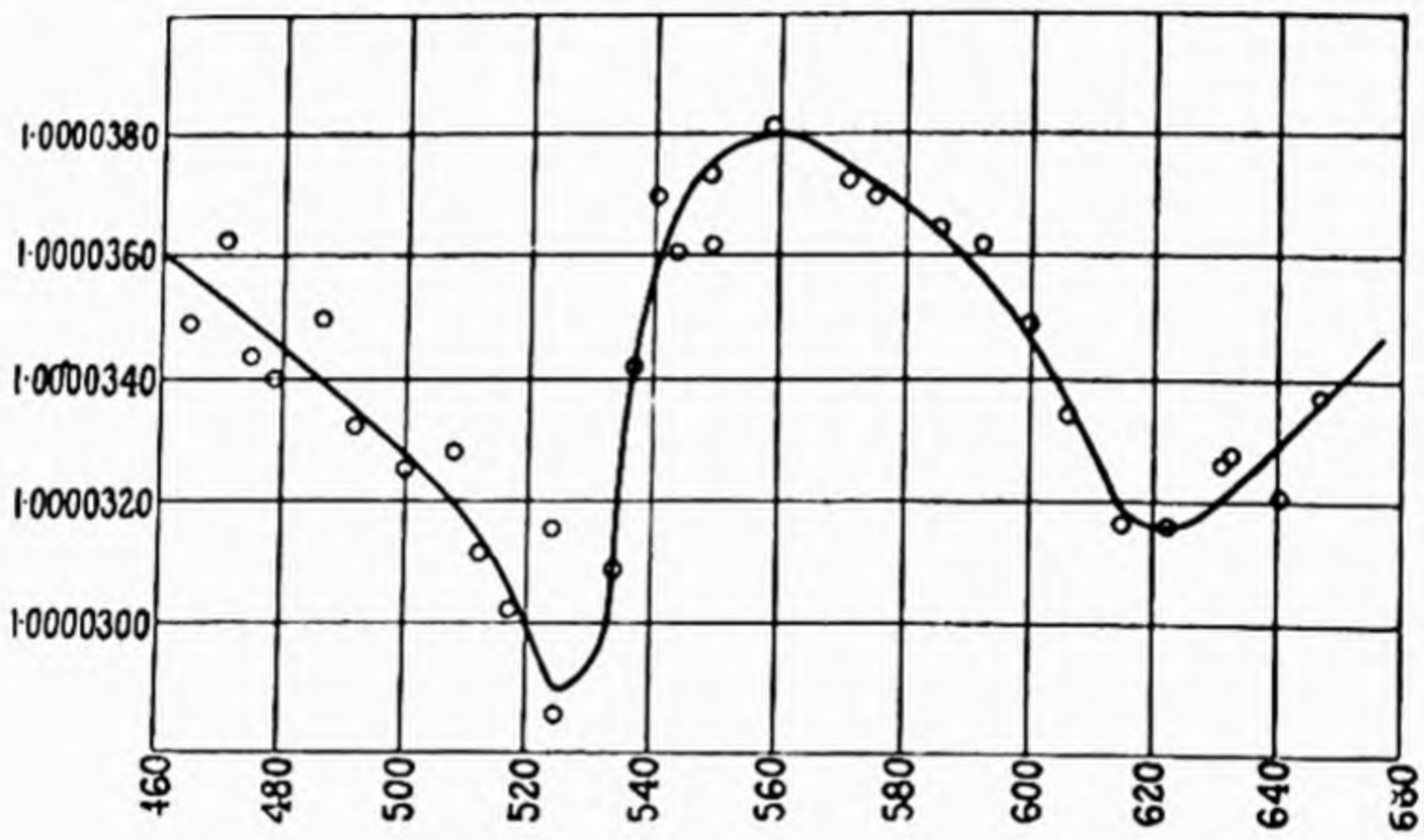


FIG. 17.

standard established by this work came as a bombshell in the spectroscopic camp. As was described in Vol. I., p. 202, the whole basis of the Rowland system was the wave-length of the D_1 line as determined by Bell, all wave-lengths being determined by the coincidence method with concave gratings in relation to that line. It had always been believed that even if the value of the wave-length of the D_1 line were in error it would only be necessary to multiply Rowland's values by a constant factor. The curve of errors given in Fig. 17 proved that this was not the case, but that there must be a periodic error which is not a function of the wave-length. There is no need to enter into a discussion of the problem that was raised and the steps that were taken by the International Union for Co-operation in Solar Research in the first instance and later by the International Astronomical Union, for this was dealt with in Vol. I., pp. 35 and 204. That which concerns us here is the fact that it was agreed that interferometer standards be set up and that these be determined by the Fabry and Perot étalon method. The modern method of work with all its re-

finements whereby these standards were established may be described, but we may, in the first place, mention certain improvements that have been made in the construction of the interferometer and of the étalon. In the case of the former, the rubber bags full of water for producing the final adjustments have been done away with, and owing to improved workmanship it has been found possible to control the fine adjustments by simple mechanical means. One of the most

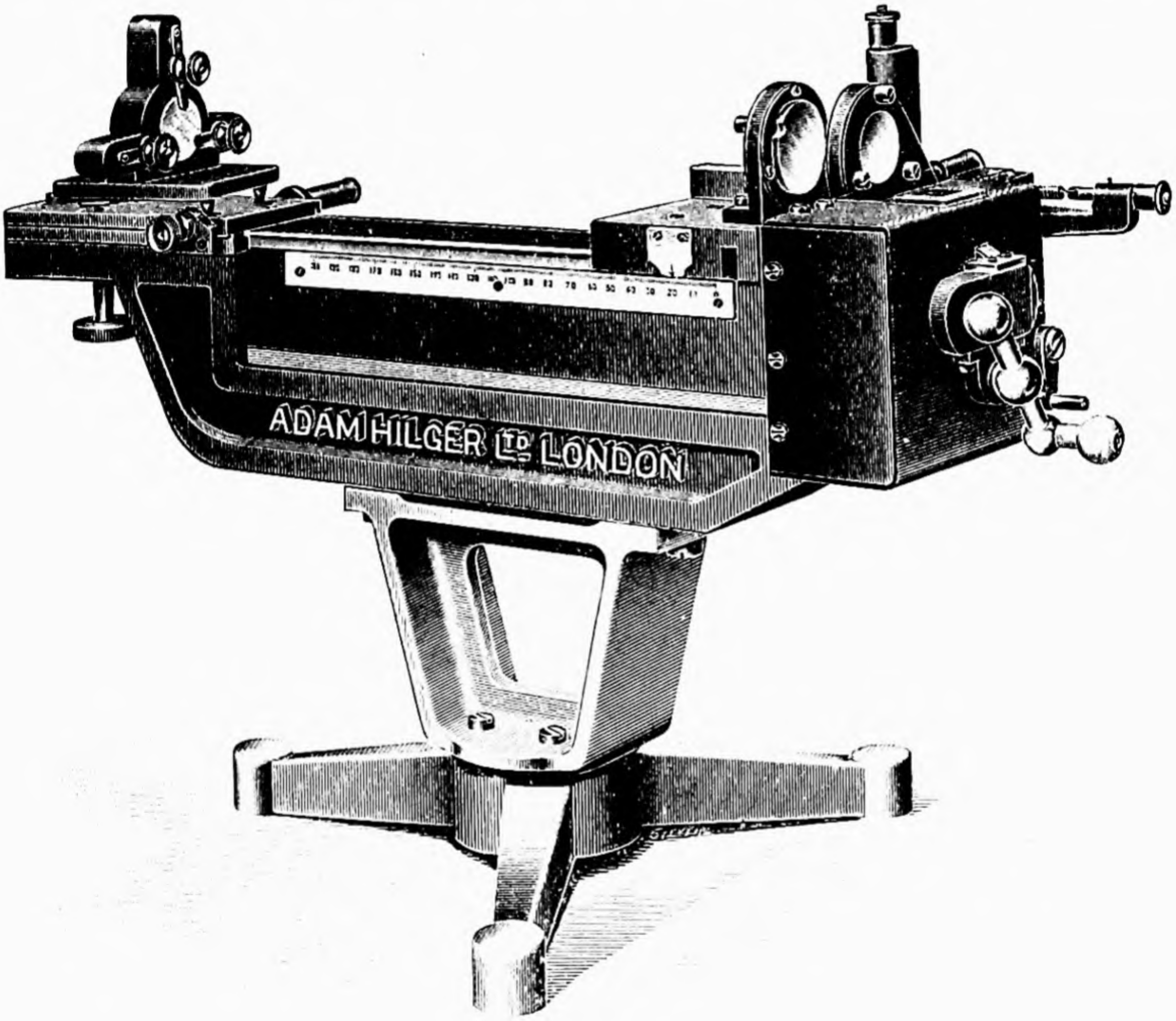


FIG. 18.

modern forms of the apparatus is shown in Fig. 18. In addition to being an interferometer this instrument has an extension for holding an étalon for the determination of its thickness, as was shown on p. 29. The instrument can therefore be used for both purposes. Then, again, the silvering of the interferometer plates by chemical means has, in many cases, given place to the deposition of the silver by cathode streams in high vacua.[1] For work in the ultra-violet

[1] Houllevigue, *Comptes Rendus*, **135**, 626 (1902).

region where silver possesses a very small reflecting power, it is necessary to use films of some other metal, and for this purpose either nickel or platinum, cathodically deposited, is very satisfactory.

In the case of the étalon, the steel distance pieces between the two interferometer plates are now replaced either by the alloy invar or by quartz.[1] The very small coefficient of thermal expansion of these two materials greatly reduces the errors caused by changes in temperature.

There is one great improvement in the method which was used by Fabry and Perot in their wave-length measurements by means of étalons, and that is the visual observation and measurement of the fringes given by a single line at a time. Apart from the tediousness

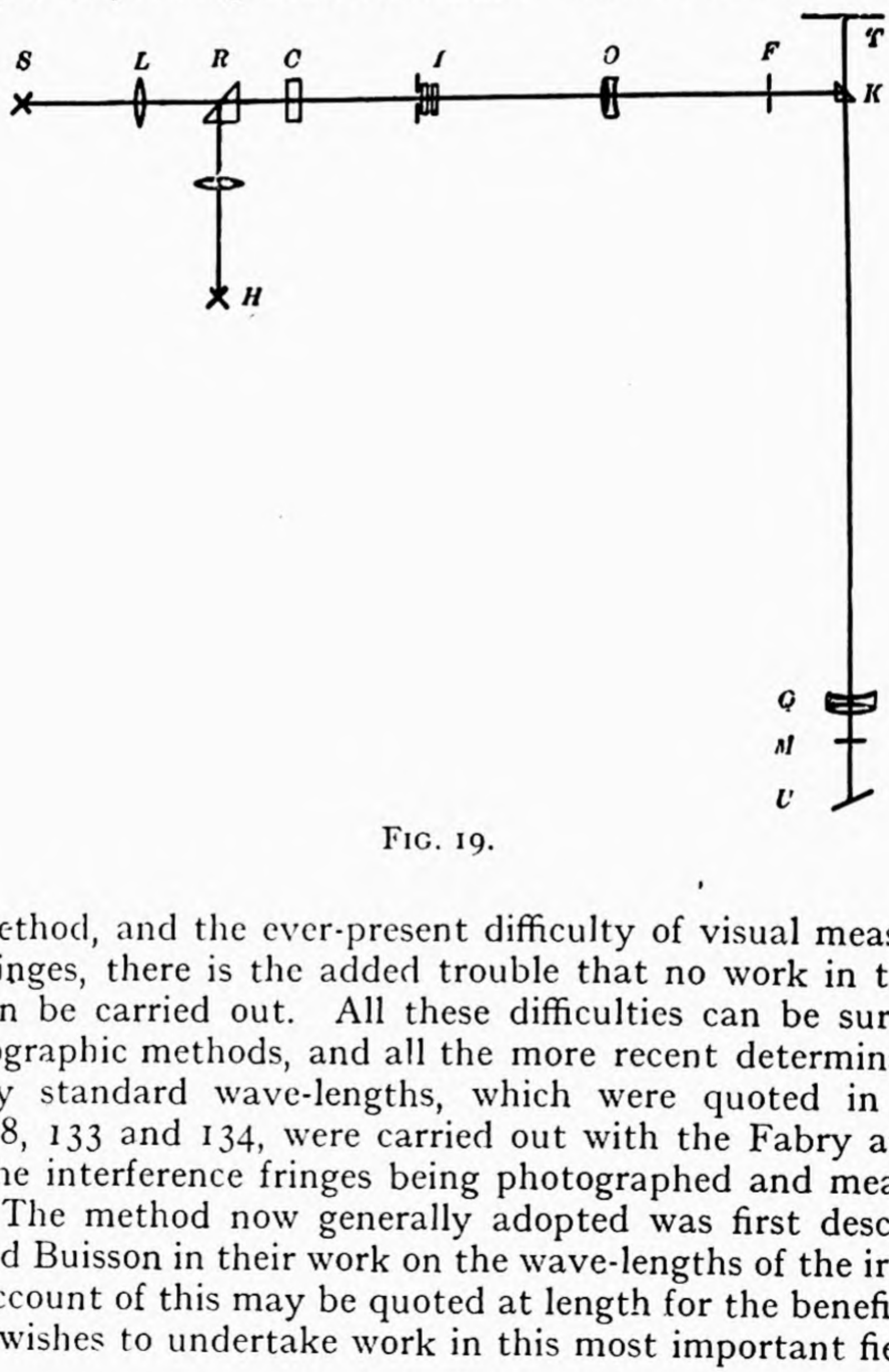


FIG. 19.

of the method, and the ever-present difficulty of visual measurement of the fringes, there is the added trouble that no work in the ultra-violet can be carried out. All these difficulties can be surmounted by photographic methods, and all the more recent determinations of secondary standard wave-lengths, which were quoted in Vol. I., pp. 37, 38, 133 and 134, were carried out with the Fabry and Perot étalon, the interference fringes being photographed and measured at leisure. The method now generally adopted was first described by Fabry and Buisson in their work on the wave-lengths of the iron lines,[2] and an account of this may be quoted at length for the benefit of anyone who wishes to undertake work in this most important field. The

[1] Rentschler, *Astrophys. Journ.*, **28,** 345 (1908).
[2] *Astrophys. Journ.*, **28,** 169 (1908).

scheme of the apparatus is shown diagrammatically in Fig. 19, where S is the source, L is a convergent lens, and C is an absorption cell in order, if necessary, to remove portions of the spectrum which are not required. The étalon is placed at I, and O is an objective, called the ring objective, which projects the interference rings upon its focal plane at F. According to this arrangement, each radiation gives its own system of rings, all of which have their centres at the same point. In order to separate the radiations, a spectrograph is employed with its slit placed in the focal plane F. A Littrow type of instrument with a plane grating is most convenient for general use; a concave grating is inadmissible owing to the astigmatism. On the photographic plate T are projected as many images of the slit as there are separate wave-lengths in the incident light, and each of these presents the result which would be obtained if the source emitted the corresponding radiation only upon the portion of the plane F which is occupied by the aperture of the slit. The latter should be of such a width as to prevent the image corresponding to the radiation to be measured from encroaching upon the adjacent images. A wide slit may be used with spectra having few lines, whilst the slit must be narrow when the spectrum is very rich in lines. The images obtained in the two cases are shown in Fig. 20.

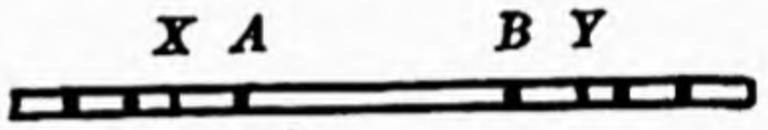


FIG. 20.

The totally reflecting prism R is used to introduce the radiation which is used as the standard of comparison. In their work Fabry and Buisson used the green mercury ray emitted by a mercury lamp placed at H. As a matter of fact, this radiation is not very satisfactory, owing to the number of satellites which it contains (see p. 182), but it was only used for the sake of convenience as an intermediary, the real standard of reference being the cadmium red ray.

It is necessary to determine the angular diameters of the rings. For this purpose the linear diameter of one of these (AB, Fig. 20) is measured, and from this the angular diameter may at once be deduced if the scale of the image is known, that is to say, the number of millimetres corresponding to a given angle. To accomplish this there are placed across the slit two metal wires which project upon each image two straight lines (XY, Fig. 20). When the diameter AB is measured there is also measured the distance XY = r. The angle corresponding to the difference XY has previously been determined, and thus there are to hand all the elements necessary for the computation.

The optical arrangement requires modification according to the spectral region studied. For rays of greater wave-length than 3600 the étalon may be made of silvered glass plates, but for smaller wave-lengths quartz plates must be used with a nickel film deposited by cathode projection. A diaphragm is used with the étalon so as to employ a field only 8 mm. in diameter, this precaution eliminating

any error which might arise from a slight lack of parallelism of the surfaces. It is obvious, too, that all the lenses must be of quartz or quartz-calcite in the case of ultra-violet rays.

In each case it is necessary to know the angular distance which corresponds to the distance apart of the two wires placed over the slit. This is directly determined for the green mercury ray by means of a telescope focussed at infinity and fitted with a micrometer eye-piece which has been previously calibrated in terms of angle with the help of a divided circle. The angle θ for any radiation, λ, is derived from the angle θ' measured for the green mercury ray by means of the formula $\theta = \theta' \frac{f'}{f}$, where f and f' are the focal distances.

In the actual determination of wave-lengths the following photographs are taken :—

1. Exposure on the mercury rings.
2. Exposure on the rings of iron.
3. Exposure on the mercury rings.

The reason for taking photographs of the mercury rings before and after the iron exposure is to eliminate the effect of temperature changes. Since the images of the cross wires on the slit are not always easily visible if they chance to fall between two bright rings, it is advisable to make two exposures with the slit illuminated by mercury and iron rays respectively after having removed the étalon.

The measurements consist in the determination of the diameters of the rings, that is AB in Fig. 20, and also of the distance apart of the reference marks. These distances do not exceed 10 mm., and the accuracy of reading under favourable circumstances is 0·01 mm. These measurements give for each iron line and the mercury line the distance between the standard marks, the diameter of the first ring and, if possible, that of the second. The angle corresponding to the distance between the standard marks is known and the order of interference at the centre of the rings can be calculated in the following way. In the case of the mercury ray, let r' be the distance between the standard mark, θ' the corresponding angle expressed in radians, and δ' the diameter of that of one of the measured rings, the number of order of which, P′, is known. The angular diameter of this ring is $\alpha' = \frac{\delta'}{r'}\theta'$. The order of interference at the centre is then

$$p' = \mathrm{P}' + \frac{\mathrm{P}'\alpha'^2}{8} = \mathrm{P}' + \frac{\mathrm{P}'}{8}\left(\frac{\delta'\theta'}{r'}\right)^2.$$

If the diameters of two rings are measured, two values of p' are obtained which ought to be identical. In general they agree to within a few thousandths. The mean is taken of the results obtained from the two exposures on the mercury ray. Owing to the presence of the observers and to the light sources, the temperature rises somewhat between the two exposures, so that the second of these gives for p' a value a few thousandths higher.

Let us consider now a ray of iron. Let λ be its wave-length, which is unknown. We know the values of r, δ, θ corresponding to the rings of this ray. The ring with diameter δ has for the number of its order the integer P, which is not yet known. We proceed to determine this by means of the known approximate value λ_1 of the wave-length λ. This value is taken from Rowland's tables, and is multiplied by 0·999967, the mean ratio between the true wave-lengths and those of Rowland. The equation $p\lambda = p'\lambda'$ upon substituting for λ its approximate value λ_1, gives an approximate value p_1 of the order of interference p. If the approximation is sufficiently close no error is introduced in the integral part. The number of the first ring is the integer next smaller than p_1, and this determines the numbers of all the rings and in particular the number P of the ring measured. We then calculate the order of interference of the centre by the formula

$$p = \mathrm{P} + \frac{\mathrm{P}}{8}\left(\frac{\delta\theta}{r}\right)^2.$$

An error of a unit in the approximate value need cause no alarm, for example, the order of interference being, say, 20,000, it would be necessary for the approximate value λ_1 to be in error by 1/20,000 in order to cause a like error. As a matter of fact, the error is much less; the fractional part of p, the order of interference as measured, differs from that of the approximate value p_1 by a quantity considerably less than unity. In general, the difference does not exceed 0·1. The orders of interference are thus determined with an uncertainty of less than 0·01. As they all are in the neighbourhood of 20,000, the relative value is less than 1/2,000,000. In the most unfavourable cases the uncertainty in the value of λ does not reach one part in 1,000,000. For a given negative, the order of interference p' relative to mercury is a constant. We calculate, once for all, the product $p'\lambda'$, which represents twice the thickness of the étalon. This thickness is thus determined with an accuracy of the order of 0·002μ.

There is still to be considered the correction for phase. We have proceeded on the assumption that the optical thickness of the air film is the same for all radiations. This is not strictly true on account of the change of phase at reflection from silver which varies very slightly with wave-length. This was discussed on p. 29, where it was shown that it is necessary to add a small correction

$$\gamma = \frac{2(e - e')}{p}.$$

The problem will be solved if for each radiation the difference $\epsilon = 2(e - e')$ is known of the doubled optical thicknesses corresponding to the two radiations λ and λ'. This difference is evidently independent of the thickness itself; λ' being fixed, it is a simple function of λ which may be determined for given surfaces once and for all. For this purpose it is sufficient to make use of interferences of a low order,

using rays the wave-length of which is closely known. With the same surfaces, let an air film be formed only a few microns in thickness in such a way that the orders of interference q and q' are not greater than about 20. These quantities being once known, we have $2e = q\lambda$ and $2e' = q'\lambda'$, and since q and q' are very small, these equations give e and e' with very great absolute precision, even though the wave-lengths are not very exactly known. The difference $\epsilon = 2(e - e')$ may be calculated, and if this is repeated for various radiations a curve may be drawn, giving ϵ as a function of λ. Since, in general, this function does not vary rapidly, it is sufficient to make the measurements for a few radiations distributed throughout the spectrum.

From this curve it is easy to plot a correction curve applicable to these silverings when employed with a given air thickness. We have

$$\gamma = \frac{\epsilon}{p} = \frac{\epsilon}{2e}\lambda.$$

The problem reduces itself to the observation for certain radiations of the orders of interference while working with a film of very small thickness. Fabry and Buisson used thicknesses of the order of 8μ, and made use of the fringes of thin plates, as being more convenient in this case than the rings at infinity. These fringes are produced by parallel light and exhibit the lines of equal thickness of the air film. On one of the silvered surfaces there was traced with a fine point several standard marks arranged along a straight line, and each consisting of two intersecting straight lines. The two silvered surfaces were then superposed, being held apart by three strips of thin tin foil placed round their edges. The whole was then tightly held in a screw clamp. By transmitted monochromatic light rectilinear fringes are seen, the distance apart of which and orientation may be varied by turning the screws of the clamp. They are thus brought into perpendicularity to the line of standards and first examined by mercury light. To each point of the film, and in particular to each standard, there corresponds with the green light a definite order of interference. The numbers of the green fringes are easily obtained by examining their coincidences with the yellow and violet fringes. The order of interference corresponding to any standard is deduced from a measurement of the distances of the standard from the neighbouring fringes.

This process is repeated for any other radiation, λ, and the order of interference determined in the same way: its fractional part by interpolation and its integral part by calculating in the first place the approximate value of q, namely, $q'\lambda'/\lambda$. We may then calculate the values of the double optical thicknesses $2e = q\lambda$ and $2e' = q'\lambda'$, and consequently $\epsilon = 2e - 2e'$.

In this computation the wave-lengths are regarded as known, but it is not necessary to know them with great precision. Supposing that we have fringes of order 40, q is determined to 1/4000, very nearly. If λ is in error by 0·1 Ångström, this will cause in $2e$ an error ten times

less than that which results from the uncertainty of q, and, therefore, negligible.

Fabry and Buisson repeated these measurements for each of the silverings that they used. They found that the properties of silverings chemically produced seemed to be always identical amongst themselves, and to depend only on the thickness. The values obtained were in the same sense and of the same order of magnitude as those indicated by Fabry and Perot. When the wave-length 3300 is approached, not only does the reflecting power rapidly diminish, but the change of phase also undergoes a rapid variation. On the contrary, the silverings obtained by cathode projection do not all behave alike as regards the size, or even the sense, of the difference ϵ.

As was stated in Vol. I., p. 36, it has been decided that all wave-lengths shall be expressed in terms of their values in dry air at 15° and under normal pressure. Variations in the condition of the air cause the wave-lengths to change in absolute value by considerable amounts. On the other hand, the ratios of wave-lengths vary by very small quantities only, for the effect is entirely due to the dispersion of air. If the index of refraction of air were constant through the spectrum, all measurements of wave-lengths would be correct as if under normal conditions, whatever might be the state of the atmosphere at the time of taking the photographs. The dispersion of air, however, is not zero, and hence a correction must be made which, although very slight, depends upon the atmospheric conditions at the time of making the negative.

Let M be the specific mass of the air under the experimental conditions, defined by the temperature t and the pressure H. Further, let λ be the wave-length of a ray under the experimental conditions, n the corresponding index of refraction of the air and λ' and n' the analogous quantities for the standard ray. The same letters with subscript zero may represent the same quantities under normal conditions, and the quantity which we wish to find is λ_0. We have measured p and p' under actual conditions, and hence have obtained $p\lambda = p'\lambda'$. The quantity $\frac{p'\lambda'_0}{p}$ is computed, which would be the normal wave-length if the air were not dispersive, and a correction is applied to this. The correction has the value

$$\eta = \lambda_0 - \frac{p'\lambda'_0}{p} = \lambda_0\left(1 - \frac{p'}{p} \times \frac{\lambda'_0}{\lambda_0}\right) = \lambda_0\left(1 - \frac{\lambda\lambda'_0}{\lambda'\lambda_0}\right),$$

but
$$\frac{\lambda}{\lambda_0} = \frac{n_0}{n} \text{ and } \frac{\lambda'}{\lambda'_0} = \frac{n'_0}{n'},$$

and hence
$$\eta = \lambda_0\left(1 - \frac{n_0 n'}{n'_0 n}\right) = \lambda_0 \frac{n'_0 n - n_0 n'}{n'_0 n},$$

in which the denominator $n'_0 n$ may be replaced by unity. Further,

$$\frac{n - 1}{M} = \frac{n_0 - 1}{M_0} \text{ and } \frac{n' - 1}{M} = \frac{n'_0 - 1}{M_0}.$$

Solving these equations for n and n', and introducing these into the expression for η,

$$\eta = \lambda_0(n_0 - n'_0)\frac{M - M_0}{M_0}.$$

The factor $\frac{M - M_0}{M_0}$, which is easy to calculate as a function of the temperature and pressure, is constant for all the rays of any one negative. Moreover, the quantity $\lambda_0(n_0 - n'_0)$ may be calculated as a function of the wave-length and plotted on a curve.

The measurement of the absolute wave-lengths of the lines in the iron spectrum was later undertaken by the Bureau of Standards in Washington, and two papers in particular may be mentioned, namely, those by Burns [1] and by Burns, Meggers, and Merrill.[2] The apparatus and method employed were the same as those used by Fabry and Buisson, and described above. Mention, however, may be made of the fact that in the second investigation, which dealt with the region 6750 to 3233, at least three interferometers were used, each having quartz plates 8 mm. in thickness with platinum films cathodically deposited. An important simplification in the determination of the phase change correction is described by Meggers and the following description may be quoted from his paper.[3]

The correction due to change of phase on reflection which must be applied to wave-lengths obtained by interference methods is usually made for each wave-length, either as a correction to the thickness of the étalon e or to the order of interference p. This correction can be made directly to the wave-lengths from their uncorrected values, as determined from a thin étalon e_1 and a thick étalon e_2. The values from e_1 will be smaller or larger than those from e_2, depending on their position in the spectrum and on the nature of the metallic film. Let a point λ' in the spectrum be chosen as a standard of wave-length and represent the measurements of another wave-length λ, as obtained from e_1 and e_2 by λ_{e_1} and λ_{e_2} respectively. Let the difference $\lambda_{e_2} - \lambda_{e_1} = c$. If the effect of phase change be regarded as zero at λ', the total correction to λ can be shown to be proportional to c.

Let $d\lambda_{e_1}$ and $d\lambda_{e_2}$ represent the phase change error in wave-length from e_1 and e_2 respectively. If the penetration of light into the films at reflection be regarded as an increase ϵ in the optical distance e between the interferometer plates, then

$$\lambda = \lambda_{e_1} + d\lambda_{e_2} = \frac{2(e_1 + \epsilon)}{p_1} = \frac{2e_1}{p_1} + \frac{2\epsilon}{p_1}$$

and

$$\lambda = \lambda_{e_2} + d\lambda_{e_2} = \frac{2(e_2 + \epsilon)}{p_2} = \frac{2e_2}{p_2} + \frac{2\epsilon}{p_2}.$$

[1] *Bureau of Standards, Bulletin* **12**, 179 (1915).
[2] *Ibid.*, **13**, 245 (1916-17).
[3] *Ibid.*, **12**, 198 (1915).

But $\lambda_{e_1} = \frac{2e_1}{p_1}$ and $\lambda_{e_2} = \frac{2e_2}{p_2}$, since the measured values of λ are always expressed in terms of the étalon thicknesses which result from the standard wave-length λ' and the orders of interference which are obtained from measurements on the rings. Consequently

$$d\lambda_{e_1} = \frac{2\epsilon}{p_1} \text{ and } d\lambda_{e_2} = \frac{2\epsilon}{p_2}.$$

Then $d\lambda_{e_1}/d\lambda_{e_2} = p_2/p_1$ and since p is directly proportional to e for a given value of λ we have

$$d\lambda_{e_1}/d\lambda_{e_2} = e_2/e_1 \quad \text{or} \quad d\lambda_{e_1} - \frac{e_2}{e_1} d\lambda_{e_2} = 0 \quad . \quad . \quad (1)$$

and

$$d\lambda_{e_1} - d\lambda_{e_2} = \lambda_{e_2} - \lambda_{e_1} = c \quad . \quad . \quad . \quad (2)$$

Subtracting (2) from (1) gives

$$d\lambda_{e_2}\left(\frac{e_2}{e_1} - 1\right) = c, \quad \text{or} \quad d\lambda_{e_2} = \frac{e_1 c}{e_2 - e_1}.$$

The phase change correction from λ' to λ for any other thickness e is then

$$\frac{e_2}{e} d\lambda_{e_2} \quad \text{or} \quad \frac{e_2}{e} \cdot \frac{e_1 c}{e_2 - e_1}.$$

In this way this error can be corrected from point to point in the spectrum.

For example, several wave-lengths in the ultra-violet portion of the spectrum of neon were measured with 2 mm. and 15 mm. étalons, using $\lambda' = 5852{\cdot}4862$ A as standard.

λ_{e_1}.	λ_{e_2}.	$\lambda_{e_1} - \lambda_{c.} = e.$
3417·888	3417·903	+ 0·015
3447·685	3447·703	0·018
3520·457	3520·472	0·015

The mean correction to λ in this region is, therefore, proportional to 0·016 A, and the amount which must be added to λ_{e_2} is

$$d\lambda_{e_2} = \frac{e_1 c}{e_2 - e_1} = \frac{2 \times 0{\cdot}016}{15 - 2} = 0{\cdot}0025 \text{ A}.$$

Thus, the mean of three measures of $\lambda = 3417 +$ with 15 mm. étalons gave $\lambda_{e_2} = 3417{\cdot}9031$, whence the true wave-length is 3417·906 to three decimal places. Similarly, several lines near $\lambda = 6500$ gave $\lambda_{e_2} - \lambda_{e_1} = c = -0{\cdot}004$, from which $d\lambda_{e_2} = 2 \times -0{\cdot}004/(15 - 2) = -0{\cdot}0005$ A. The mean of three measures of $\lambda = 6532 +$ with 15 mm. étalons gave $\lambda_{e_2} = 6532{\cdot}8834$ A. The correct wave-length is therefore 6532·883 A.

The method used by Fabry and Buisson to determine the phase change correction consists in finding the difference in optical differences between the interferometer plates for different wave-lengths.

This can be done by finding the relatively small orders of interference p and p' for two wave-lengths λ and λ' at the same point of an interferometer arranged with a thin, wedge-shaped air space so as to give localised straight line fringes. Then the distance in double optical thicknesses e and e' at this point for λ and λ' is $\epsilon = 2(e - e') = p\lambda - p'\lambda'$. From their curve ϵ between $\lambda = 6500$ and $\lambda = 3460$ was equal to $21\mu\mu$ or 210 A. If the correction to wave-length be regarded as zero at $\lambda = 6500$, the correction to $\lambda' = 3460$ from a 15 mm. étalon becomes $210 \times 3460/30 \times 10^7 = 0{\cdot}0024$ A. The above measures on the neon lines give the correction over this interval as $0{\cdot}0025 + 0{\cdot}0005 = 0{\cdot}0030$ A. This difference may represent a real change in the film with time.

Whenever ϵ varies linearly with λ, as in the case of these films, the correction to any wave-length λ is $d\lambda_{e_2}/(\lambda - \lambda')$ Ångström for each Ångström, which separates λ from the standard wave-length used in the measurement. Thus the mean of three measures of $\lambda = 7032 +$ gave $\lambda_{e_2} = 7032{\cdot}4143$ A. The correction is $0{\cdot}0030$ $(5852 - 7032)/(6500 - 3460) = -0{\cdot}0012$, and the true wave-length is $7031{\cdot}413$ A.

The difference $\lambda_{e_2} - \lambda_{e_1} = c$, upon which the correction depends, is larger the greater is e_2 and the smaller is e_1. The accuracy of this determination is thus increased as the order of interference in e_2 becomes larger. The use of a source of light which will give a high order of interference is therefore to be recommended. Since it is always advisable to use as large as possible an étalon in interferometer measurements of wave-lengths, sufficient data are immediately at hand from which to make the phase change correction to the wave-lengths measured if an additional set of measurements is made with a thinner étalon.

I cannot refrain from giving a short description of two very interesting applications of interferometry to astronomy. In one of these the Fabry and Perot étalon was used to examine the light from the great nebula in Orion, and in the second the Michelson interferometer was used to determine the relative masses of the components of a double star Capella and their distance apart, and also to determine the linear diameter of the star Betelgeux.

In the study of the great nebula in Orion,[1] not only were the wave-lengths of the radiations emitted by this nebula determined with great accuracy, but the variations found in the wave-length of the blue line of hydrogen led to determinations of the velocity with which this stupendous mass of gas is moving in the line of sight. The results show that not only is the mass travelling as a whole, but that it also is in a state of rotation. The change in wave-length caused by motion in the line of sight, or radial velocity as it is generally called by astronomers, will be fully dealt with in Vol. IV., but the work on this nebula may well find mention here owing to the use of the étalon and the

[1] Buisson, Fabry, and Bourget, *J. de Phys.*, **4**, 357 (1914).

surmounting of the difficulty caused by the small angular diameter of the nebula.

The nebula gives little light and has an apparent angular diameter of only a few minutes. In producing the interference fringes it is necessary to avoid using the rays from different parts of the nebula, and consequently an image of the nebula must be obtained on the photographic plate at the same time as the fringes. If the interferometer were directed towards the nebula and an objective projected the fringes on to the plate, an image of the nebula would be obtained. This arrangement is, however, useless, since the diameter of the nebula image would be smaller than the first interference ring. The following arrangement was adopted. A concave mirror, 80 cm. in diameter and 450 cm. focus, projected an image of the nebula in a plane F. Behind F at a distance of 5·6 cm. were placed two achromatic lenses, the focal length of the combination being 5·6 cm. The angular enlargement thus produced was $450/5{\cdot}6 = 80$. The light beam then passed through the étalon with an annular aperture of 1 cm. in diameter. Immediately behind the étalon was a short focus lens with a clear aperture of 1 cm. and a focal length of 4·5 cm. The photographic plate was placed in the focal plane of this lens and on the plate were formed the images of the interference rings and of the nebula, the latter being eighty times as large as it would be if the lens were directed towards the nebula in the heavens. In the focal plane of the concave mirror a pair of cross hairs was placed, and the image of these on the plate served as a landmark in the measurement of the photographs.

The whole of the measurements were referred to the violet ray of mercury. Three photographs were always taken, one with the nebula and one with the violet ray of mercury taken before and after the former. The problem is to determine the wave-length of the ray from the nebula which gives the rings. This may be a known hydrogen ray, but with its wave-length modified by radial velocity, or it may be an unknown ray. As far as the measurements are concerned, the problem is the same in the two cases. If the nebula has only a translatory motion the problem is very simple, for the wave-length will be the same at every point and the interference rings will be perfectly circular. The diameter of the rings are measured without determining the position of the centre of the system. If, as is actually the case, there are differences of radial velocity at various parts of the nebula the matter becomes very complicated, for it is impossible to speak of a single value for the wave-length. The rings are then deformed and it is necessary to refer each measurement to the true centre of the rings, that is to say, the centre of the ring system given by the mercury ray. This centre is determined with the mercury ray by the use of the cross hairs previously mentioned, the central point being co-ordinated with respect to the two hairs and their intersection.

To determine the radial velocities it was necessary to use a ray of known wave-length present in the nebula spectrum, and the line H_γ

was selected, the wave-length of this line being first determined in the laboratory with reference to the mercury ray with the same interference apparatus.

All the observations of the nebula were made of the region of the trapezium. In the region surrounding the trapezium the mean radial velocity with reference to the sun is + 15·8 km. per second. This is the mean of the values found for 58 points in twelve directions round the trapezium. There are also changes in radial velocity from point to point, for this enormous mass of gas is not in relative repose. In certain regions the rings are deformed, indicating that small portions of the nebula vary in radial velocity by as much as 10 km. per second. Such movements exhibit themselves in the region S.E. of the trapezium. Besides this, there are large movements of the whole, since the N.E. region is receding at the rate of 5 km. per second compared with the mean velocity, while the S.W. region is approaching at about the same velocity. In fine, the part of the nebula studied has a kind of rotation round the line N.W.-S.E., but there are also many irregularities.

The pair of ultra-violet rays attributed to the unknown element nebulium were measured with a very high degree of accuracy, the wave-lengths being 3726·100 and 3728·838 A. respectively. No known element gives these rays, the suggestion that they might be characteristic of oxygen being now disproved. By determination of the order of interference at which the visibility of the fringes vanishes it is possible to obtain a value for the atomic weight. Étalons with greater and greater thickness of path were used, until the fringes were no longer visible. In the case of Hγ the order of interference at the limit of visibility was very near 10,000, whereas in the case of the ultra-violet pair of rays of nebulium it was probably about 16,500. The ratio of the two atomic weights is therefore $(16{,}500/10{,}000)^2 = 2{\cdot}74$, and, therefore, the atomic weight of nebulium is about 3.

The green ray, $\lambda = 5006$, is also due to an unknown gas and, although the measurements were not so accurate, the fringes vanished when the order of interference was less than 16,500, and, therefore, the atomic weight of this gas is very probably less than 3. It is of some interest to note that the Rydberg classification of the elements calls for two elements between hydrogen and helium with atomic weights of 2 and 3 respectively.

The temperature of the luminous gas can be calculated from the formula

$$N = 1{\cdot}22 \times 10^6 \times \sqrt{\frac{m}{T}},$$

where N is the order of interference when the fringes vanish, m is the atomic weight, and T is the temperature. Using the value of 10,000 for N in the case of the hydrogen ray the maximum temperature is found to be 15,000°. It must be remembered that every contributory cause tends to diminish the visibility of the fringes, such as

any difference in radial velocity between the gaseous masses at the same point, with the result that the value found for T will be too high.

The second line of investigation I will describe is an application of the Michelson interferometer, and this work has very great importance, since apart from its intrinsic interest it reveals the remarkable possibilities of this instrument. In one of his early papers Michelson [1] described a method for the measurement of the angular magnitude of astronomical objects, such as the diameter of planetoids and satellites, and the distance between double stars, when these are beyond the powers of the largest telescopes. The method consists in utilising only the two portions of a large objective at opposite ends of a diameter.[2] The interference fringes at the focus under these conditions will be a series of equidistant interference bands, which are most distinct with a source subtending an infinitesimal angle. For an object presenting an appreciable angle the visibility is less and may become zero, the exact relation being readily expressed for any given distribution of light in the source. Thus, if $\phi(\alpha)d\alpha$ represent the intensity of a strip of the source of angular width $d\alpha$, and s the distance between the apertures (supposed small compared with s), and if $\mathrm{P} = \int\phi(\alpha)d\alpha$, $\mathrm{C} = \int\phi(\alpha)d\alpha \cos 2\pi\frac{s}{\lambda}\alpha$, and $\mathrm{S} = \int\phi(\alpha)d\alpha \sin 2\pi\frac{s}{\lambda}\alpha$, then the visibility of the interference fringes is

$$\mathrm{V} = \frac{\sqrt{\mathrm{C}^2 + \mathrm{S}^2}}{\mathrm{P}}.$$

Thus for a double star, the brightness of whose components is in the ratio $1 : r$ and whose angular diameter is α,

$$\mathrm{V} = \frac{\sqrt{1 + r^2 + 2r\cos 2\pi\frac{\mathrm{S}}{\lambda}\alpha}}{1 + r}.$$

For equal components this reduces to $\cos\frac{\pi s\alpha}{\lambda}$ which vanishes when $\alpha = \frac{\lambda}{2s}$. Accordingly, this angle can be accurately measured when it is only half the limit of resolution of the full-apertured telescope.

Again, by comparing the visibility at maximum and minimum, the ratio of the brightness of the component stars may be found from

$$r = \frac{\mathrm{V}_1 - \mathrm{V}_2}{\mathrm{V}_1 + \mathrm{V}_2}.$$

For a uniformly illuminated disc

$$\mathrm{V} = \int_0^1 \sqrt{1 + \omega^2}\cos\omega n d\omega,$$

[1] *Phil. Mag.*, **30**, 1 (1890).

[2] *Astrophys. Journ.*, **51**, 257 (1920).

where $n = \frac{\pi s \alpha}{\lambda}$, α being the angular diameter. For such an object the fringes vanish when $\alpha = 1{\cdot}22\lambda/s$.

Michelson found by tests with the 40-inch refracting telescope at the Yerkes Observatory, and the 60-inch and 100-inch reflectors at Mount Wilson that clear and relatively steady fringes can be obtained even when the "seeing" is bad. The method was then applied by Anderson [1] to the measurement of the separation of the components of the double star Capella, using the 100-inch reflector at Mount Wilson. This star was selected because its spectroscopic orbit and parallax leads to a value of 0·05 second of arc for the angular separation of its components, which would be easy to measure with the interferometer applied to the 100-inch telescope.

The actual method of making the measurements is described in detail by Anderson, and the following account is taken from his paper. Let the light from a star fall upon two apertures placed in front of the telescope objective or mirror. Let the width of each aperture measured along the line joining their centres be d, and the distance between their centres be D. The shape of the diffraction pattern seen in the focal plane of the telescope will depend upon that of the apertures, but the important thing is its dimensions in the direction of the line joining the two apertures, and this, in angular measure, as seen from a distance equal to the equivalent focal length of the telescope, is $\alpha = 2C\lambda/d$. The intensity being, say, unity at the centre of the pattern, falls to the first zero value at an angle $\alpha/2$ from this point. C is a factor depending upon the shape of the apertures, and for rectangular slits C = 1, whilst for circular apertures C = 1·22 nearly. Upon the diffraction pattern will appear the interference fringes, these being at right angles to the line joining the two apertures. The angular distance between two bright fringes is λ/D. Hence the number of fringes which can be seen on the central diffraction disc depends on the ratio D/d and is equal to 2CD/d. If this number is greater than 10, the fringes farthest from the centre will, in general, be invisible in white light, because of the overlapping of the different colours.

Let us assume that the apparatus is pointed at a double star, the angular separation of the components of which is β. If β is larger than $2C\lambda/d$, two separate diffraction patterns will be seen, each with its own system of interference fringes. When β is less than $2C\lambda/d$ the patterns will overlap more or less, and if β is just equal to λ/2D and the position-angle of the double star is the same as that of the line joining the two apertures, the conditions are such that a bright fringe due to one component falls on a dark fringe due to the other component, that is to say, the two fringe systems are out of step by just one-half a fringe. Hence, if the two component stars are of the same intensity, the visibility of the fringes near the centre of the

[1] *Astrophys. Journ.*, **51**, 263 (1920).

pattern will be zero. It is, of course, evident that minima of visibility will occur when $\beta = N\lambda/2D$, where N is any odd integer. Hence it may be seen that the interferometer will resolve two stars, the angular separation of which is $\lambda/2D$, just as a circular telescope objective of diameter D will resolve two stars the separation of which is $1{\cdot}22\lambda/D$, that is to say, the resolving power of the interferometer is rather more than twice that of a telescope of the same aperture. It may also be remembered that useful measurements may be made with the interferometer, even when the angular separation is much less than $\lambda/2D$.

Let D_0 denote the smallest value of D which will cause the fringes to disappear for a double star having equal components. If we choose D a little larger than D_0, so that $D_0 = D \cos \theta$, it is evident that the fringes will be visible when the position-angle of the apertures is the same as that of the double star. If, now, the interferometer be rotated through an angle $\pm \theta$, the fringes will just disappear, and the same thing will happen when the instrument is rotated through an angle $180° \pm \theta$. For any value of D greater than D_0 there are, therefore, four values of the position-angle, for each of which the fringes disappear or have minimum visibility according as the two components of the double star are of equal or unequal intensity. From these four position-angles and the known value D one can obviously find the value of D_0 and the position-angle of the double star.

The method just described was employed in the work on Capella. As a rule a complete observation included three complete rotations of the interferometer for each of three values of D, making a total of 36 readings of position-angle. The values of D were so chosen that θ, as defined above, should lie between 30° and 50°. Under these conditions, and with reasonably good seeing, the probable error of a single reading should not exceed 3°. It is probable that with a little practice a good observer will be able to reduce the probable error of a single setting to about 1°. The corresponding error in the distance is about 1·8 per cent.

Given a suitable arrangement for measuring the visibility of the fringes, the following method of observation may be used: Choose a value of D smaller than D_0. Determine the visibility at position-angles differing from each other by, say, 15° all the way round the circle. If the object is a double star, the visibility will show two maxima and two minima in a revolution. This will also be true if the object has the form of a luminous surface longer in one dimension than at right angles thereto. Further measurements will, however, readily distinguish between this case and that of a double star. Repeat the series twice, using two other values of D. The data thus obtained should be sufficient to determine both position angle and distance of the double star, with a high degree of accuracy, and without requiring a value of D as large as D_0.

Having found D_0 as explained above, we need to know only λ in

order to compute β, since $\beta = \lambda/2D_0$. The value of λ for the sun was found from laboratory measurements, using as an artificial double star two small round holes illuminated by sunlight reflected from freshly-silvered mirrors. The constants of the apparatus were determined by direct measurements, and also by observations on the artificial double star illuminated by very nearly monochromatic light of known wavc-length. The results from two series of observations with sunlight were $\lambda = 5498$ and 5500 A. It seems safe, therefore, to use for a G-type star $\lambda = 5500$ A, and this value was employed in reducing the observations of Capella.

In this connection it is important to bear in mind the rôle played by the background on which the interference pattern was observed. On one day an observation of Capella was made in full daylight. The observation was very easy to make, but on being reduced, using the value of λ given above, the distance between the components came out approximately 10 per cent. too small. A little consideration shows that this might have been predicted, for the skylight, being relatively very rich in blue light, would reduce the visibility of the blue fringes much more than that of the yellow or red fringes, thus resulting in a considerable increase in the value of the effective wavelength.

The measurements gave the angular distance between the two components as 0·05249 second. From the spectroscopic elements the period was calculated to be 104·006 days, the parallax to be 0·06 second, the distance between the centres of the two components to be 130,924,000 km., and their relative masses to be 4·62 and 3·65 times that of the sun, respectively. These values have been slightly modified by Merrill [1] as the result of further observations carried out at Mount Wilson with Anderson's method. He gives the period as 104·022 days, the angular separation as 0·05360 second, and the parallax as 0·0632 second.

The first application of this method to the measurement of the diameter of a star was made by Michelson and Pease,[2] and a brief description may be given of the construction of the interferometer.

It had previously been found that the interference fringes remained at full visibility with the slits separated by the diameter of the 100-inch reflector at Mount Wilson, and consequently an interferometer was built with movable outer mirrors in order to make observations with separations as great as 20 feet. A diagram of the apparatus is shown in Fig. 21, and the instrument mounted on the Cassegrain cage of the 100-inch telescope is shown in Fig. 22. The interferometer beam was constructed of two 10-inch steel channels with flanges turned inwards, separated by pieces of 12-inch channel, and covered on the bottom with $\frac{3}{16}$ steel plate, all riveted securely together. To reduce the weight, holes were cut wherever the removal of the metal would not weaken the structure. The inner edges of the top flanges were planed

[1] *Astrophys. Journ.*, **56**, 40 (1922). [2] *Ibid.*, **53**, 249 (1921).

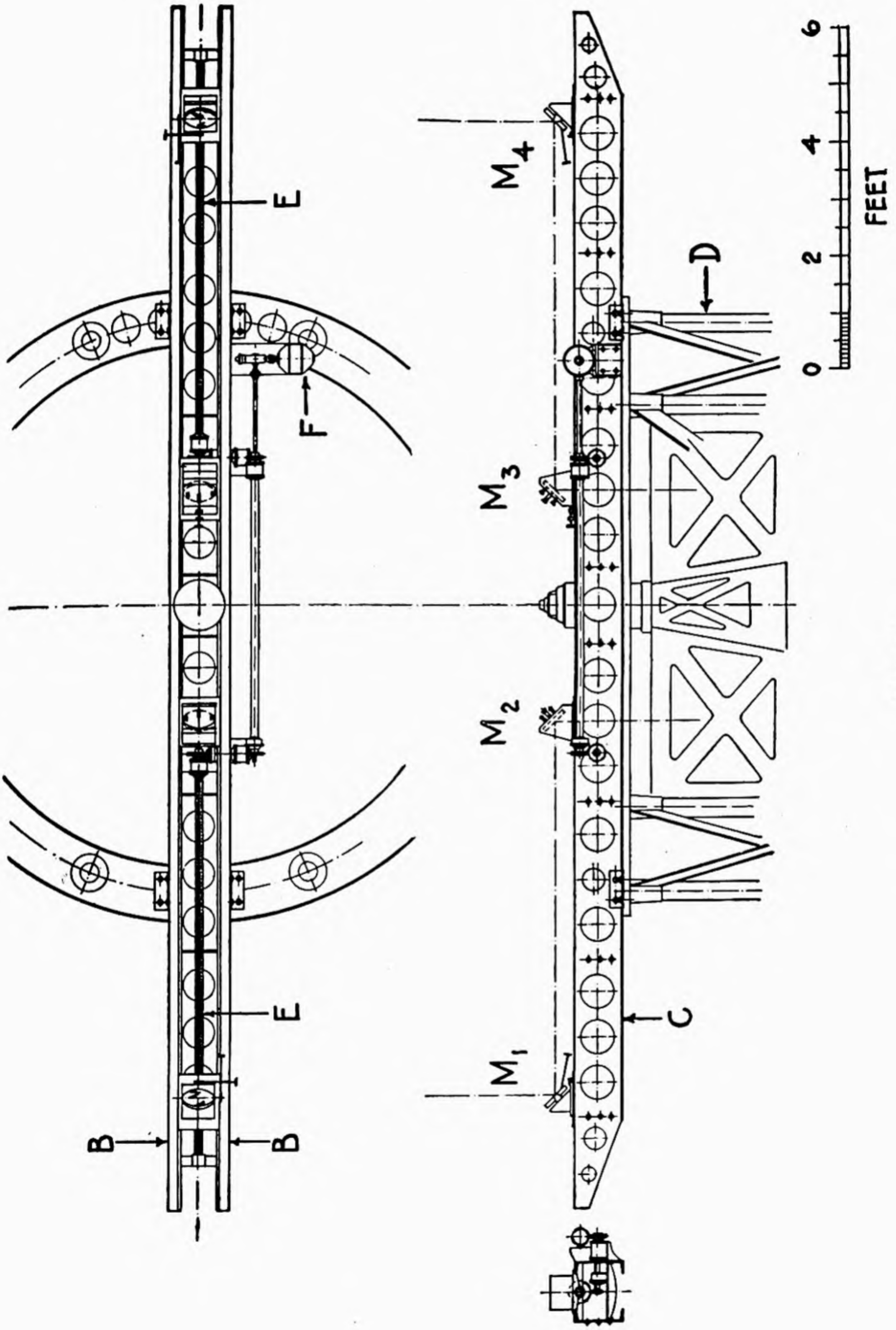


FIG. 21.

true to 0·001 inch, the beam being supported as it was to be mounted on the telescope.

The four mirrors, M_1, M_2, M_3, M_4, about 6 inches in diameter, inclined 45° to the base, are mounted on slides. M_2 and M_3 are permanently fixed, except that M_3 has a motion of several millimetres along its slide parallel to the beam. The nearly constant separation of M_2 and M_3 by about 45 inches gives the fringe pattern a fixed spacing of 0·02 mm., easily visible with a magnification of 1600. The outside mirrors M_1 and M_4 can be shifted along the beam, their distances from M_2 and M_3 being kept equal. Two pencils from the

FIG. 22.

star are reflected from the outer mirrors M_1 and M_4 to the inner mirrors M_2 and M_3, and thence follow the ordinary course in the telescope. Before this apparatus was completed by the provision of means for continuously altering the position of the outside mirrors, some observations were made on α Orionis (Betelgeux), which is known to be very large. When the separation of the pencils was 121 inches, no fringes could be seen, although tests on other stars showed that the instrument was in perfect focus. Assuming the effective wave-length to be $\lambda = 5750$ A, this separation for the first minimum visibility gives the angular diameter from the formula $\alpha = 1{\cdot}22\lambda/b$ as $0{\cdot}04''/\pm 0{\cdot}005''$. With a parallax of $0{\cdot}018''$, the linear diameter of the star

proves to be 240,000,000 miles, which is slightly less than the diameter of the orbit of Mars. This calculation is based on the stellar disc being uniformly illuminated, and if the disc is darkened towards the limb the diameter would be greater by about 17 per cent.

One of the uses to which Fabry and Perot applied their interferometer was the examination of the structure of spectrum lines, and their method of work was indicated above on p. 20. Two very simple pieces of interference apparatus may be described which are especially suited for the examination of the structure of the finest spectrum lines. Whilst it is not possible with either of these apparatus to determine the wave-lengths of secondary standards, the relative wave-lengths of the components of a single line may be accurately measured with reference to that of the principal component. The first of these interferometers was devised by Lummer and this instrument can be best understood from a diagram, which is given in Fig. 23.[1]

AB is a glass plate 5·4 mm. thick and 20 cm. long, of which the upper and lower sides are made as plane as possible, and parallel to one another. C is a prism cemented to the plate; a beam of parallel light falls upon C, as is shown. The ray undergoes a series of reflections inside the glass plate, and at each reflection some of the light is

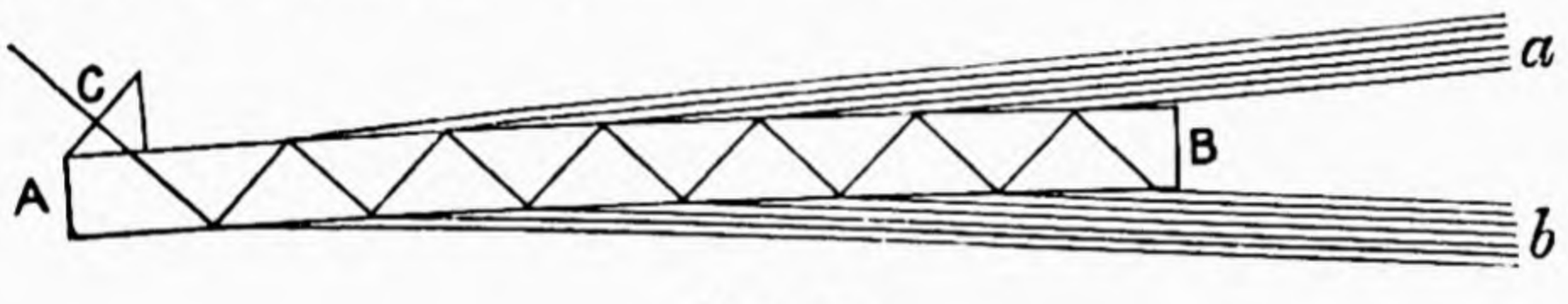


FIG. 23.

refracted into the air, and the two pencils *a* and *b* are formed, one by the rays escaping from the upper side, and the other by the rays escaping from the lower side of the plate. These two pencils enter the telescope, and the interference rings are observed at the focus of the objective. Lummer and Gehrcke have employed this apparatus for the resolution of the lines of the spectrum of mercury.

Gehrcke [2] has shown that a considerable advantage is gained by using two of these plane-parallel interference plates which are set at right angles to one another, so that a series of bright point maxima are seen. In this way the false maxima due to errors in the plate are readily differentiated from the real maxima, and hence certain errors which may arise from the use of a plate that is not quite perfect may be eliminated. In a later paper Gehrcke and von Baeyer [3] show how small differences of wave-length may be measured with these crossed plates (see p. 182).

A similar type of interferometer has also been described by Barnes;[4] this is a reflecting instrument, and is shown in Fig. 24. It consists of

[1] *Verh. d. Deutsch. Phys. Ges.*, **7**, 85 (1901), and *Berl. Ber.*, 11 (1902).
[2] *Ibid.*, **13**, 236 (1905).
[3] *Ann. d. Physik*, **2**, 269 (1906).
[4] *Astrophys. Journ.*, **19**, 190 (1904).

two perfectly plane parallel pieces of glass; the under surface of the upper plate is heavily silvered and carefully polished, whilst the lower plate is almost completely silvered on its upper side, so that its reflecting power is about 0·9. The light is incident upon the upper plate, as is shown, and, due to multiple reflections between the silver plates, we have transmitted a number of rays whose path differences are in arithmetical progression. The rays escaping through the lower

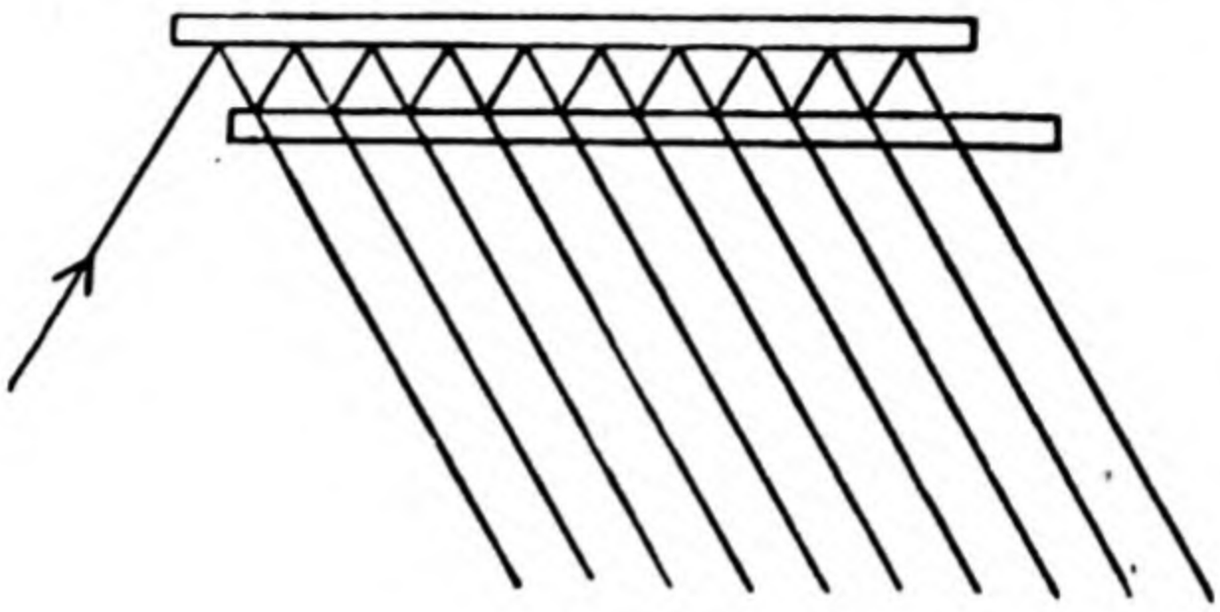


FIG. 24.

plate are focussed by a lens, and the interference fringes are examined in the focal plane. The two plates are mounted upon an interferometer similar to that described for Michelson's apparatus (see Fig. 1, p. 3). Barnes claims that with this apparatus the bright interference bands are much stronger than those obtained with the Fabry and Perot method, and hence the weaker components are more readily seen.

CHAPTER II.

METHODS OF ILLUMINATION.

In general, it may be said that spectroscopic observations fall naturally into two main divisions, namely, emission spectra and absorption spectra. The two divisions differ so much in their technique and in their nature that they must be dealt with entirely separately. The term emission spectra covers a very large field indeed, for not only does it include the methods of excitation of atoms and molecules so that they emit their characteristic radiations, and also the nature of those radiations, but in addition to these two sub-divisions there must be included the existence of series in line and band spectra, and the effect of magnetic and electric fields on emission spectra. The subject of emission spectra is thus a very large one, and it will be preferable to discuss the whole with all its ramifications before the great field of absorption spectra is introduced.

It will be advisable before commencing any account of the former to indicate the method which it is proposed to adopt. It is obvious that the methods of illumination or excitation must take first place in our sequence. These methods may be divided into four classes, namely, flame spectra, including temperature emission spectra, arc spectra, spark spectra, and lastly fluorescence and phosphorescence spectra. The first three involve the excitation of the atoms or molecules in the gaseous state, whilst the last refer in the majority of cases to the luminescence of liquids or solids. It will be convenient to deal with the last-mentioned phenomena separately, because they would seem to be of a different type.

I propose, therefore, in one chapter to discuss the three principal methods of illumination, and in a second chapter to speak of the radiations emitted. Then will follow a description of the work on fluorescence and phosphorescence. Since one of the most important weapons of spectroscopic technique is the photographic plate, a few pages may then be devoted to this important side of our work. This will conclude the description of the methods employed in emission spectra. Then will follow chapters on series in line spectra, series in emission band spectra, the Zeeman effect, and the Stark effect. As there still remains the great branch of absorption spectra I have found it impossible to include the whole in a single second volume. In order to give an adequate treatment of these various branches of our

subject, it has been decided to divide the whole into three volumes. The present volume will include the description of the methods used in emission spectra, the third volume will include the two chapters on series of lines in emission spectra and those on the Zeeman and Stark effects, whilst the fourth volume will be devoted to absorption spectra and to the shift of spectrum lines by pressure and by motion in the line of sight. This subdivision, rendered necessary by the great advances made during the last thirteen years, will probably be found the most convenient. In accordance with the scheme outlined there follows at once an account of flame spectra, arc spectra, and spark spectra, including the electric discharge through gases under reduced pressure.

Flame Spectra.—The Bunsen flame itself is a convenient method for the production of spectra, but under ordinary circumstances its use is restricted to a few more or less volatile metallic salts. The method of introduction of the salt into the flame is familiar enough to any one who has practised chemical analysis, where the colours given to a Bunsen flame by certain salts are made use of in the scheme of work. A platinum wire is taken, and a small loop is made on the end; the looped end of the wire is then heated to redness in the Bunsen flame to remove all traces of deposit therefrom—notably sodium salts from the fingers. The wire is heated as long as any yellow tinge is given to the flame; it is best in the case of a wire which has been previously used to moisten the end with hydrochloric acid. When the wire is clean it may be dipped into a solution of the salt of the metal whose spectrum is required, and then put into the outer mantle of the Bunsen flame; at once the characteristic flame coloration will be produced, and this may be examined in the spectroscope in the ordinary way. It is best in these cases to use the chlorides of the metals, as these salts are volatile, and therefore give better results.

The metals which give the flame colorations in this simple way are, lithium, sodium, potassium, rubidium, and cæsium; barium, strontium, and calcium. Some other substances give flame colorations, but not of so decided a nature as to render this method feasible for the investigation of their flame spectra. It will readily be understood that the flame coloration as produced above is not very lasting, and so can hardly be used when one requires a continuous illumination. Under these circumstances the arrangement devised by Mitscherlich [1] may be employed, as shown in Fig. 25, in which the wick *c* consists of a bunch of very fine platinum wires or asbestos threads. The tube *a* is filled with a solution of the required salt, and, when the wick is put into the flame, a very constant coloration is produced. It is a great advantage to dissolve

FIG. 25.

[1] *Pogg. Ann.*, **116**, 499 (1862).

some ammonium acetate along with the required salt; this causes the solution to flow better along the wick. Mitscherlich recommends that 1 part of a concentrated salt solution be mixed with 20 parts of a 15 per cent. solution of ammonium acetate.

Another convenient apparatus has been used by Eder and Valenta;[1] two metal discs, about 6 to 8 inches in diameter, are mounted upon the same axle and screwed together with a ring of platinum gauze between their edges; this gauze projects about 1 inch all the way round. The axle of the wheel is mounted at an inclination of 45°; the upper edge of the gauze projects into a powerful Bunsen burner, and the lower into a solution of the required metallic salt, placed in a shallow dish. When in use the disc is rotated at a uniform speed by means of clockwork; this apparatus will give an illumination which lasts as long as there is solution in the dish.

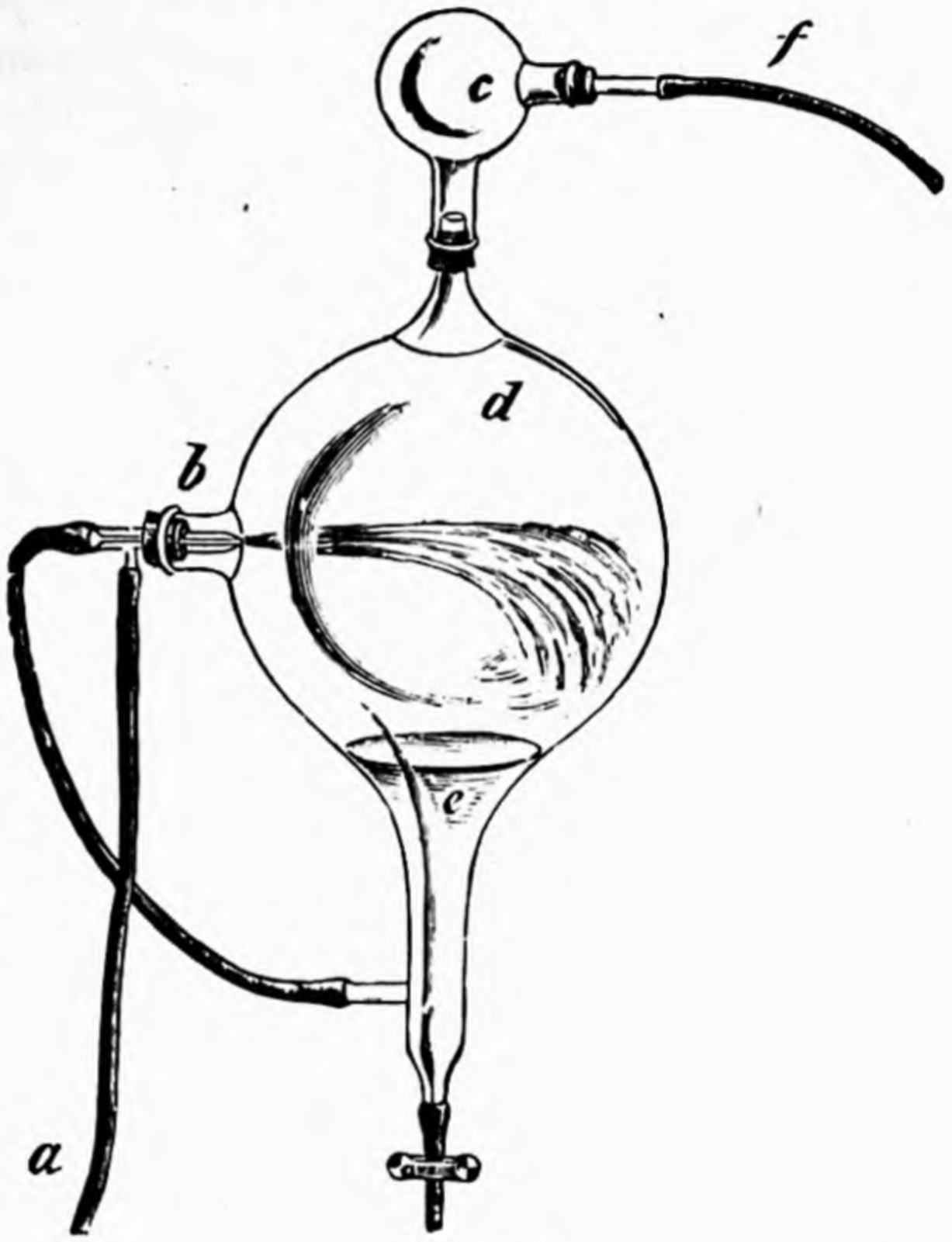


FIG. 26.

Several spraying apparatus have also been employed for this purpose, amongst which one may be described, namely, that used by Gouy.[2] In this type of apparatus the salt solution in a state of fine spray is carried along by a current of air and fed into the draught holes at the bottom of a Bunsen burner. A diagram of Gouy's apparatus is shown in Fig. 26, in which *b* represents the spraying apparatus; this consists of two tubes, one inside the other. A current of air is forced in through the tube *a*, and the spray is carried into the vessel *d*; the heavier drops fall to the bottom, while the air current passes through *c* and is conveyed by the tube *f* to the Bunsen burner. The liquid at *e* passes to the spraying apparatus through the connecting tube; the same liquid is therefore used over and over again, for it is only the finest particles which are carried away by the air stream.

With this apparatus de Watteville[3] has succeeded in obtaining the flame spectrum of mercury by using an aqueous solution of either

[1] *Wiener Denksch.*, **60**, 468 (1893). [2] *Ann. Chim. et Phys.*, **18**, 5 (1879).
[3] *Comptes Rendus*, **142**, 269 (1906).

the acetate or the cyanide. It is interesting to note that only one line is visible in this spectrum, *viz.* $\lambda = 2536{\cdot}72$, seeing that the other members of the second group of Mendeléeff's table, magnesium, calcium, zinc, strontium, cadmium and barium also possess one spectrum line which surpasses the others in intensity. The explanation of this phenomenon will be given in Volume III., Chapter I.

Reference may be made here to the characteristic blue-green colour which is produced when sodium chloride is thrown on to a clear burning coal or coke fire. The same coloration is generally visible when logs from old wooden ships are burned. The coloration is due in each case to copper, this being present in coal as copper pyrites, and in the case of the ship's logs its presence is due to the copper bolts or nails used in the construction of the ship. Of the copper salts the halides are the only ones which are volatile in low temperature flames. In the absence of chlorides the copper salts remain unvolatilised, but in the presence of sodium chloride, copper chloride is volatilised, giving the characteristic blue-green colour to the flame. This phenomenon has at times puzzled those who expect to see the well-known yellow coloration when they throw common salt on to a coke fire.

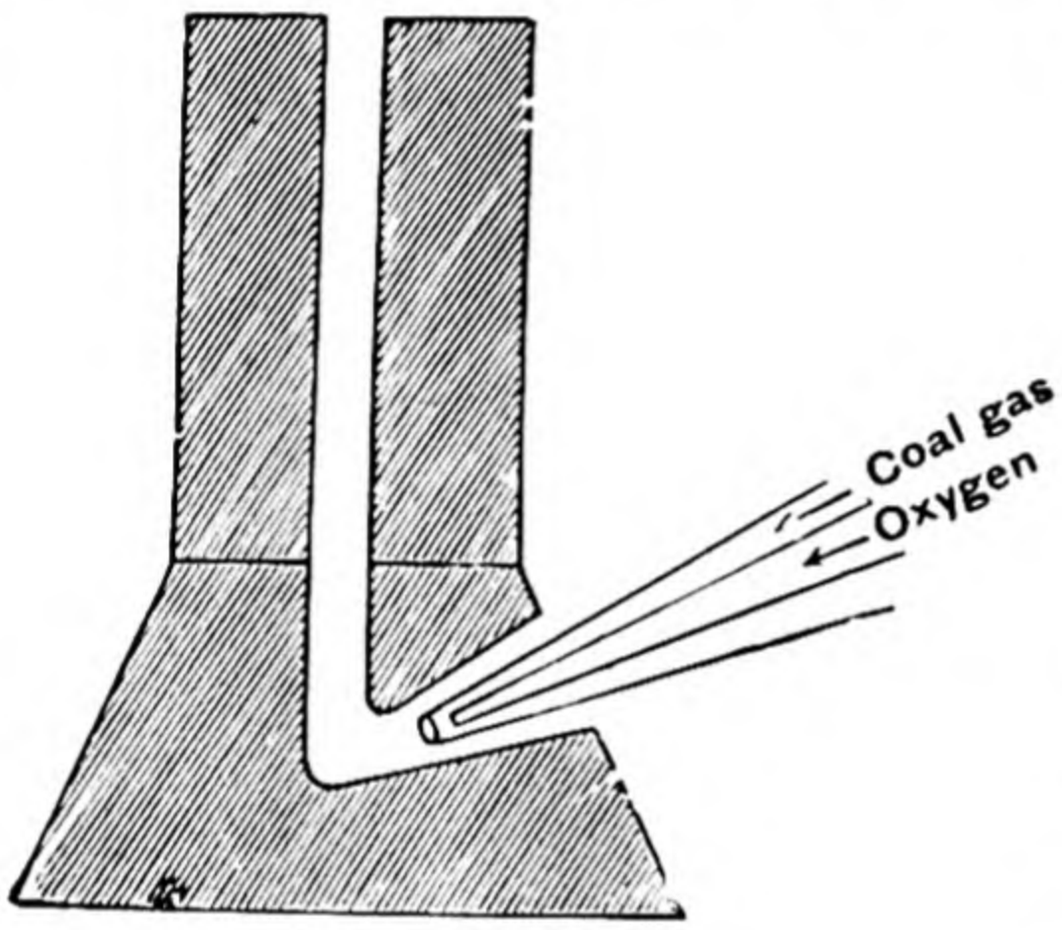


FIG. 27.

In cases where the Bunsen flame has not a sufficiently high temperature to give the spectrum of a metallic salt, the oxyhydrogen blowpipe may be used. One of the methods of work with this blow-pipe is as follows: A block of lime is bored as shown in Fig. 27, which represents it in sectional elevation. The mouth of the blowpipe is pushed into the lower hole, and the flame coming out of the top orifice is examined. The substance is put at the bottom of the boring, where the flame can play directly upon it. This apparatus was used by Lockyer and Roberts Austen,[1] and by Liveing and Dewar.[2] Hartley,[3] who has carried out a great number of investigations on flame spectra, has employed thin strips of cyanite as supports for the substance under examination, which were simply held in the upright blowpipe flame; also, when possible, the substance is very finely powdered and made into small cylinders, which are held in the flame.

In a later paper Hartley[4] suggests the use of either strips of

[1] *Proc. Roy. Soc.*, **23**, 344 (1875). [2] *Ibid.*, **28**, 352 (1879).
[3] *Phil. Trans.*, **185**, A, pp. 161 and 1047 (1894).
[4] *Proc. Roy. Soc.* (Dublin), **11**, **19**, 237 (1907).

cyanite or strips of a mixture of carborundum and porcelain clay, which has been fired at a high temperature. Very good results are also obtained by the use of quartz fibres or rods. The best burner for the purpose is, in Hartley's opinion, the Mecke burner, with or without a blast. When it is required to obtain a lasting chloride spectrum he suggests the feeding of the burner with coal gas containing a little chloroform vapour.

In special cases where very high temperatures are required the oxy-acetylene flame may be substituted for the oxy-hydrogen flame. This was used by Hemsalech and de Watteville [1] in some of their investigations, and amongst the very interesting results obtained by these experimenters may be mentioned the spectrum of calcium as given by this high temperature flame. This spectrum is very rich in the arc lines of this element and the relative intensities of the lines are very similar to those obtained by King with his electric resistance furnace (see p. 62).

It must not be forgotten that these high temperature flames have their own characteristic spectra, which consists of bands. The spectra of the flames given by the combustion of certain gaseous mixtures have been examined by Reis [2] and a knowledge of the band groups emitted is of some importance to those who utilise such flames for the production of flame spectra. The pairs of gases used were ammonia-oxygen, cyanogen-oxygen, cyanogen-air, acetylene-oxygen, hydrogen-oxygen, hydrogen-air, coal-gas-air. The gases were mixed in the jet just before being burnt.

The oxygen-acetylene flame has been used with great success by de Gramont in his work on analysis by spectroscopic methods.[3] This work will be dealt with on p. 148, and the only point which concerns us here is the technique of flame spectra. The two gases are burnt in the ordinary mixed burner which is used in commercial practice for cutting or welding. The flame has the highest temperature of any which can be used with convenience (the cyanogen-oxygen flame having a higher temperature), and is very much better than the ordinary oxy-hydrogen flame.

The oxy-acetylene flame exhibits, of course, the water vapour bands which have their heads at $\lambda = 3064$, 2811, 2608, and 2449, and are degraded towards the red. In de Gramont's own work on spectrographic analysis the most important region of the spectrum lies on the long wave-length side of the first water vapour band, and although this band is degraded towards the red, its component lines are sufficiently weak at $\lambda = 3200$ as in no way to interfere with the more refrangible of those lines used in this analytical work.

Not only can the oxy-acetylene flame be used for obtaining the flame spectra of ordinary substances, but de Gramont describes its use with minerals, such, for example, as chromite and lepidolite. He

[1] *Comptes Rendus*, **149**, 1112, 1369 (1909).
[2] *Deutsch. Phys. Ges. Verh.*, **15**, 1247 (1913).
[3] *Comptes Rendus*, **157**, 1364 (1913); **166**, 477 (1918); **176**, 1104 (1923).

points out that in general this method is not so universally applicable as the condensed spark discharge, but that it is particularly serviceable for the recognition of the presence of the following metals: the alkali and alkaline earth metals, copper, silver, gallium, indium, thallium, chromium, manganese, iron, cobalt, nickel, tin, lead, and bismuth. Whilst it is true that magnesium, zinc, cadmium, and mercury give a few lines in this flame, but under less satisfactory conditions than do the preceding metals, the same lines as given by the flame are also found in the arc and spark spectra of the above elements, but the lines in the former are less numerous and they do not extend so far into the ultra-violet.

There are, on the other hand, several elements which do not furnish characteristic line spectra in the oxy-acetylene flame. The rare earth metals, except ytterbium, which gives the line $\lambda = 3988$, do not exhibit their lines, but some give band spectra, which are well developed in the case of lanthanum and yttrium. Amongst the elements which cannot be detected by flame spectra methods are all the non-metals, the rare earths, titanium, zirconium, thorium, vanadium, niobium, tantalum, molybdenum, tungsten, and uranium. The method, therefore, is a restricted one, but within its limitations it possesses many advantages. De Gramont gives several instances of minerals which he has successfully examined by their spectra, as given by the oxy-acetylene flame. For example, a lepidolite from Madagascar revealed the presence of all the alkali metals, aluminium, gallium, and iron, whilst muscovite from the same region did not contain either lithium or cæsium. He has also, by this method, proved the presence of nickel and manganese in certain chromites, chromium in topaz, copper in Ceylon moonstone, etc. This method of flame spectra, therefore, must rank as one of the most useful to the spectroscopist whose interest lies in the analytical side of the subject.

It is very important to note that many metals give banded spectra in the high temperature flames as well as their characteristic line spectra. This phenomenon is very characteristically shown in the cases of copper, silver, gold, magnesium, zinc, cadmium, aluminium, indium, and thallium. These banded spectra were observed by Hartley and Ramage,[1] who concluded that the bands are characteristic of the metal, and not of their oxides, as had previously been suggested. The reasons which led Hartley and Ramage to this conclusion were that banded spectra are given by metals which are (1) easily oxidised to non-volatile oxides, (2) easily oxidisable to volatile oxides, (3) not oxidisable at the temperature of the flame. It was shown, however, by Basquin [2] that the same bands as those observed by Hartley and Ramage are given by the arc between poles of the metals in an atmosphere of hydrogen, which at once suggests

[1] *Trans. Roy. Soc.* (Dublin), **7**, 339 (1901).
[2] *Proc. Amer. Acad. Sci.*, **37**, 161 (1901).

that the bands are characteristic of hydride of the metal. This view was upheld by Fowler and by Olmsted, who carried out very valuable work on these banded spectra. Fowler [1] investigated the magnesium bands given by the arc in an atmosphere of hydrogen and published an accurate series of measurements of their wave-lengths between $\lambda = 5621$ and 4371. Olmsted [2] measured the calcium bands obtained in the same way, whilst the strontium and barium bands were examined by Eagle.[3] In addition to these, we have also the band spectrum which is given by titanium and was measured by Fowler,[4] who attributed this spectrum to titanium dioxide.

These banded spectra given by elements in the flame or arc present considerable interest for more than one reason. In the first place, as will be shown in the chapter dealing with these phenomena, they cannot be due to elementary atoms, since the modern theory of atomic spectra, enunciated by Bohr, has established the fact that they must consist of line spectra. In other words, a band spectrum must be characteristic of a molecule, and for this reason the conclusions as to the molecular origin of these band spectra are fully in accord with the Bohr theory. It may be added that conclusive evidence as to magnesium hydride, calcium hydride, and titanium oxide being the radiating particles, was brought forward by King, as will be described in the following section.

In the second place, the band spectra due to the last three compound molecules have an added interest in that it has been established that these bands are present in the spectra of sun spots. Indeed, it was shown by Adams [5] that these three spectra are sufficient to account for the bands appearing in the spectra of sun spots.

Turning once again to the methods of obtaining flame spectra mention may be made of a device which was devised by Hemsalech and de Watteville, and described in a series of papers.[6] They claim that the method is applicable in cases where the substance is not sufficiently volatile in the ordinary flames, or is especially valuable. The condensed electric spark is passed between two electrodes of a metal which are enclosed in a small glass bulb, a current of air is passed through the bulb and is then fed into either a Bunsen burner or an oxy-hydrogen flame, as the case may be. Substances other than metals can be dealt with in a similar way. In place of the electric spark a carbon arc is used, and for the lower electrode, which is made the positive, a hollow carbon rod is used. Into this hollow is packed the substance under examination, together with some cement. For the ultra-violet region, an intimate mixture of three parts of boron tri-oxide with one part of the substance is melted and poured into the hollow rod. For the visible region, two parts of the substance are well

[1] *Phil. Trans.*, A, **209**, 447 (1909).
[2] *Astrophys. Journ.*, **27**, 66 (1908).
[3] *Ibid.*, **30**, 231 (1909).
[4] *Proc. Roy. Soc.*, A, **79**, 509 (1907).
[5] *Astrophys. Journ.*, **30**, 86 (1909).
[6] *Comptes Rendus*, **144**, 1338 (1907); **145**, 1266 (1907); **146**, 748, 859, 1389 (1908); **150**, 329 (1910).

mixed with one part of asbestos and sodium silicate cement, the mixture being packed into the hollow rod. As in the previous case, the arc is enclosed in a small glass bulb, through which a current of dry air is passed and then fed into the flame.

There would seem to be no particular advantage in this method of excitation, since the spectrum of the spark or arc might equally well be examined. On the other hand, the spark or arc serves as a source of very minute particles, which are subsequently excited by the flame, but it must be noted that the flame spectrum obtained by this method shows the enhanced lines of the element when the spark is used. Hemsalech and de Watteville draw attention to the striking resemblance between the flame spectrum of iron obtained by their method and the spectrum of the star α Cygni.

Electrical Resistance Furnace Spectra.—A very valuable and important series of investigations have been carried out by A. S. King in the Pasadena laboratory of the Mount Wilson Observatory on the excitation of metallic spectra by volatilisation of the metals in a graphite tube electrically heated to a very high temperature. This work was undertaken with the view of investigating the conditions under which the various spectrum lines are excited, a knowledge of this being of manifest importance from the point of view of astrophysics. As will be shown in Volume III., Chapter I., the temperature classification of spectrum lines of some of the more complex spectra, such as that of manganese and iron, has rendered signal service in the more recent work on spectral series.

King,[1] in designing his electric furnace, had the following requirements in mind :—

1. The apparatus should give a long uniformly-heated column of vapour which might be brought to a temperature not far below that of the electric arc.

2. The temperature must be subject to regulation so that, other conditions being constant, the direct effect of temperature may be observed.

3. The conditions surrounding the luminous vapour must be subject to control, in order to observe the effect of changes in the nature and pressure of the surrounding atmosphere.

4. The possibility of measuring absorption when white light is passed through the heated vapour.

A tube resistance furnace was employed, namely, a carbon or graphite tube, heated by an electric current, which was supported horizontally and contained the substance to be investigated. Manifestly this tube must be protected from contact with air, and the method adopted was to surround the tube with an outer chamber, which was either exhausted or filled with an inactive gas. Further, the outer chamber was made sufficiently strong to stand high pressures.

The construction of this apparatus may be briefly described. The

[1] *Astrophys. Journ.*, **28**, 300 (1908).

essential parts of the furnace were constructed in the form of a cartridge attached to one of the heads of a steel cylinder which was built to stand strong pressures. In Fig. 28 is shown a photograph of the arrangement adopted. A half-cylinder of iron, screwed firmly to the

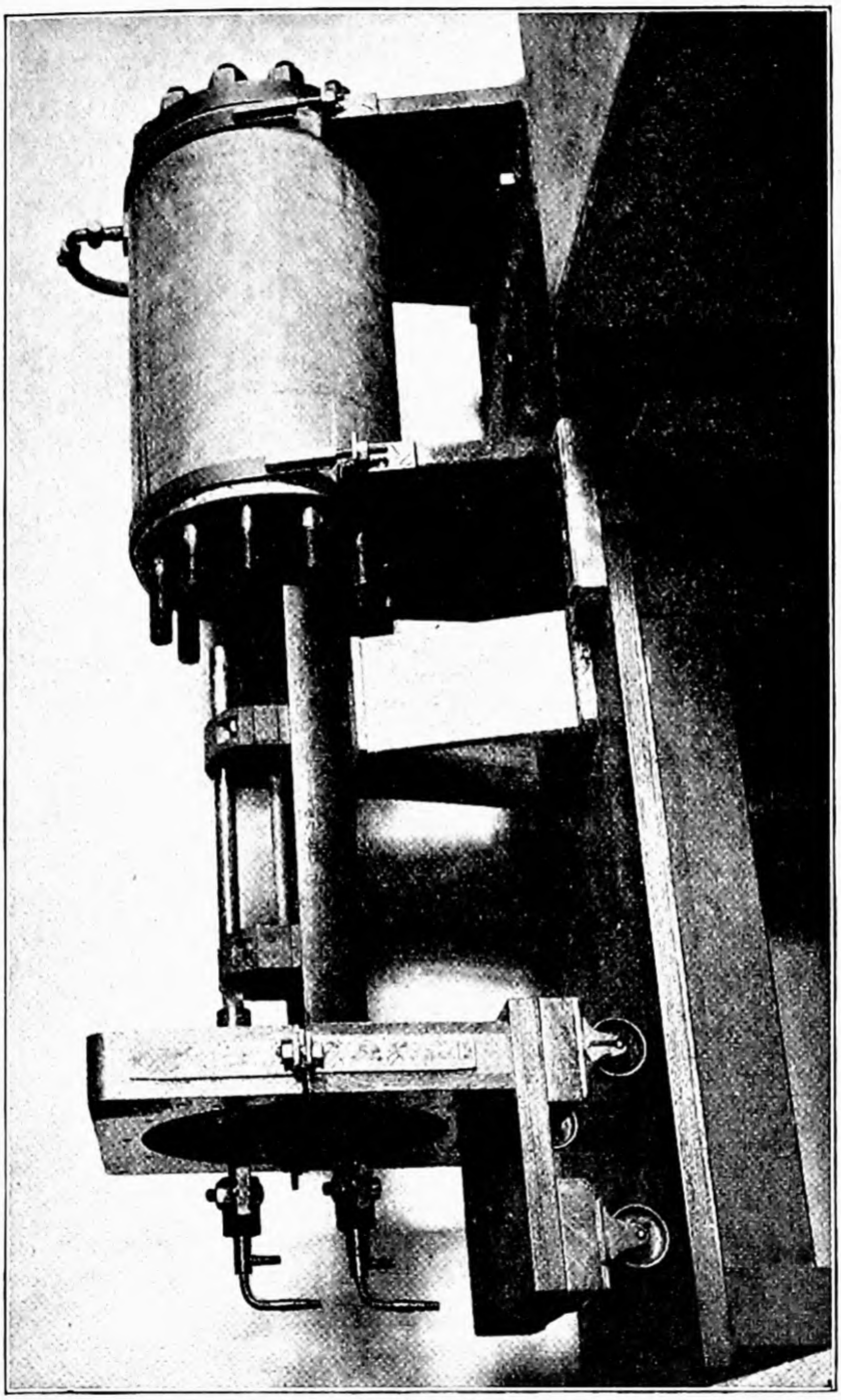


FIG. 28.

head of the pressure chamber, contains two graphite blocks which hold the ends of the horizontal resistance tube and make contact between these ends and the electrodes. These electrodes are tubular, and pass through the steel head. The graphite blocks are 2 inches thick, 6 inches wide at the middle, and in three sections. The lower

electrode is attached to the block nearer to the steel head, and this block has a channel cut in it to allow the upper electrode to pass without touching it. The sections of the blocks are bolted together with vertical bolts, and this establishes firm contact between the copper electrodes and the ends of the resistance tube. The graphite blocks are insulated from the iron half-cylinder by sheets of mica or asbestos.

The maximum length of resistance tube is 22 inches, with 18 inches heated, but King usually employed tubes 12 inches long, with 9 inches to be heated between the blocks.

A very important matter is the heat insulation of the resistance tube, and this is effected by means of carborundum powder. A carbon tube was made by boring out a block of carbon, $\frac{1}{2}$ inch shorter than the distance between the graphite blocks, with a hole having a diameter $\frac{1}{4}$ inch larger than the resistance tube. The carbon block was then turned down in a lathe until a tube was obtained with walls not thicker than is necessary to secure strength. This tube was then cut longitudinally into two halves, so that it could be placed round the resistance tube after the latter had been mounted into position. The annular space between the two tubes was filled with carborundum powder, and the outer carbon tube was completely covered with this powder, stiff sheets of mica being fixed at the sides of the iron half-cylinder to enable this to be done.

The electrodes pass through the steel head in insulated bushings, and consist each of two concentric copper tubes, with diameters $\frac{3}{4}$ and $\frac{1}{2}$ inch, respectively. Each electrode is plugged at the ends and a stream of water is maintained in the annular space between the two concentric tubes in each electrode.

The best material for the resistance tubes is Acheson graphite, though King did use at times moulded carbon tubes. The objection to the use of the latter is that they must be heated two or three times before they give good results, the tubes being cooled and cleaned between each heating. Considerable quantities of water vapour and organic matter are given off during this preliminary treatment, and the latter "cracked" and deposited slag at the ends of the tubes, this slag having to be cleared away. Further, the carbon is changed to graphite under the influence of the high temperature, with a resulting large change in electrical conductivity. There is also considerable liability on the part of the carbon to give strong impurity spectra. These objections, however, disappear almost entirely after the repeated treatment.

Acheson graphite is much more satisfactory, and in the greater part of his work King used tubes of this material turned to $\frac{23}{32}$ inch outside diameter, and $\frac{1}{2}$-inch bore.

The steel chamber is also shown in Fig. 28, and consisted of a cylinder with an internal diameter of 8 inches and walls $1\frac{1}{2}$ inches thick, carrying end flanges 3 inches thick and 2 inches wide. Each flange carried twelve $1\frac{1}{4}$-inch bolts, whereby the two steel heads are

attached. Each head has screwed into the centre a bronze plug carrying an observation window, the metal round the window in each case being kept cool by means of a special water jacket. The head at the back of the instrument has attached tubes for inlet and outlet

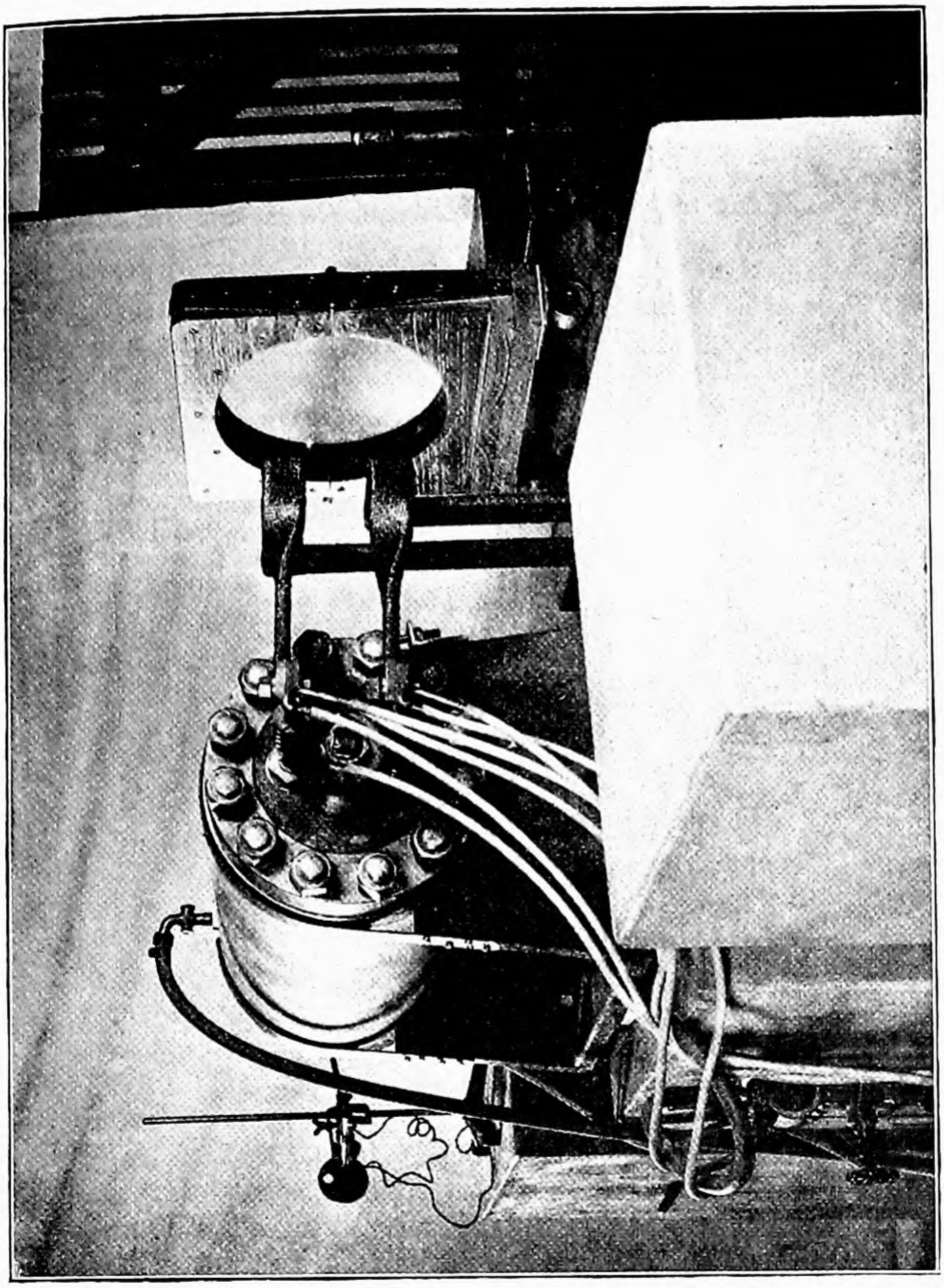


FIG. 29.

of gases and a tube for connection to the compression pump. The whole chamber is jacketed by a cylinder of galvanised iron, which is riveted to the flanges of the heads. Water is circulated through the jacket, efficient cooling being very necessary.

The electric current was obtained from a 50-kilowatt transformer,

supplied with current at 2000 volts, and giving 5, 10, 20, and 30 volts. No other resistance than that of the graphite tube was used, four different temperature limits being obtained with the above voltages. The temperature of the resistance tube was measured with a Wanner pyrometer, and the measurements obtained were sufficiently concordant to give reliable values for the approximate temperatures, which were as follows :—

5 volts . .	1700°-1800°.
10 ,, . .	2400°-2500°.
20 ,, . .	2850°-2950°.
30 ,, . .	3015°.

These temperatures naturally depend on the dimensions of the resistance tube used, and are given here in order to indicate the range which King was able to secure in his work.

The apparatus, as assembled, is shown in Fig. 29.

Certain modifications were introduced in the construction of this furnace during the course of King's work. For example, the graphite blocks were replaced by bronze blocks with central bushes of graphite, each block and bush being made in two sections, which were bolted together after the resistance tube was placed in position.

As designed above the furnace can be used either for high pressures or for very low pressures. A considerable amount of work was carried out with the apparatus after it had been exhausted, and for this particular type of investigation a more convenient form was subsequently adopted, and this is shown in Fig. 30. The hood is ground flat on its lower surface, so that an air-tight fitting is made on placing the hood on the base plate. One of the bronze blocks with its connections for water cooling and the graphite bush is shown in the photograph.

It was also found to be of great advantage in the work under reduced pressure to discard the outer graphite tube and insulating material placed round the resistance tube. In the absence of the heat insulation the equilibrium temperature is obtained much more quickly, and, further, when this is reached the temperature varies very little. It is much easier in this way to maintain constant conditions during an exposure, since the use of the insulating jacket causes the temperature slowly to rise for some time, so that a reduction of the voltage or occasional breaking of the current becomes necessary to guard against too great a temperature variation during the exposure.

Owing to the fact that the two ends of the resistance tube are open, the radiation from the heated vapour can be observed from either end. In actual practice the rays from one end of the tube are focussed on to the slit of a large spectrograph, an image of the interior of the tube being formed, and a diaphragm is used to cut off the rays from the walls of the tube. For the sake of comparison the arc spectrum of the element under investigation is photographed on the same plate. In order to achieve this, the arc is set up behind the

furnace, so that the light therefrom passes through the resistance tube to the slit of the large spectrograph. It was also possible to make visual observations of the spectrum emitted by the vapour

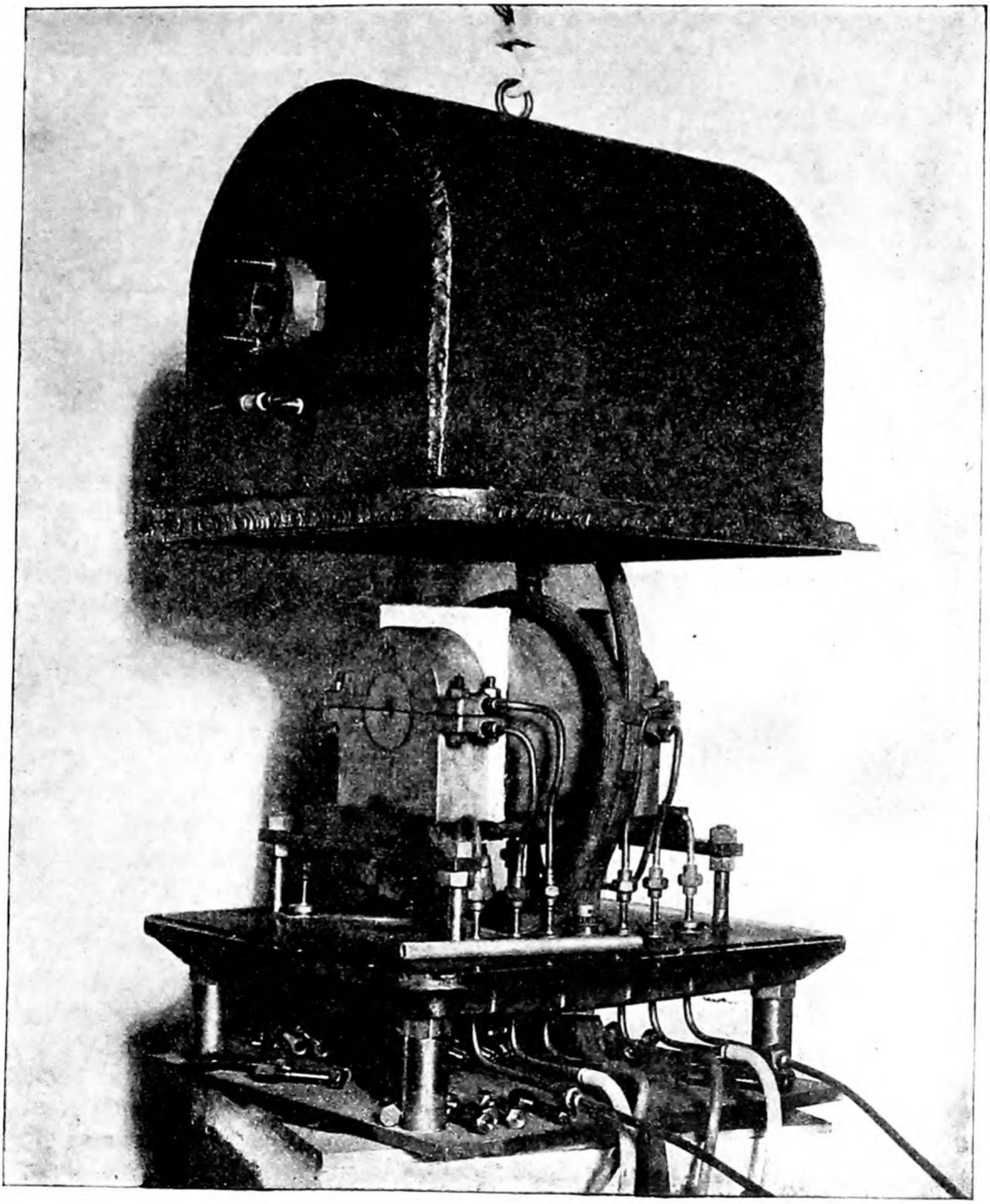


FIG. 30.

during an experiment through the window at the back end of the furnace, and, further, the temperature measurements were made by observation through this window.

The spectrograph employed was of the Littrow type, a plane grating being used during portions of the work and at other times a concave grating.

King has carried out many observations with this electric furnace, and the following may be described. His first investigation [1] dealt with the calcium lines $\lambda = 3969$ and 3934 (H and K in the solar spectrum), and $\lambda = 4227$ (g in the solar spectrum). The last-mentioned line is well recognised as one of the most characteristic lines appearing in the flame spectrum of calcium, whereas the H and K lines are generally considered to be more of the type of lines which are present in the spark spectrum. In the case of very hot flames, such as the oxy-hydrogen flame, fed with calcium, the H and K lines appear in the central core, but they are weak as compared with the $\lambda = 4227$ line, and are absent from the outermost portion, which shows the 4227 line alone. The same gradation occurs in the arc, since with a moderate current the H and K lines are much stronger than the $\lambda = 4227$ line, whilst in the outer flame of the arc the reverse is the case.

The results obtained with the electric furnace showed at once, as indeed was to be expected, that the line $\lambda = 4227$ is a low temperature line. It makes its appearance at a low temperature, and is not proportionally strengthened as the temperature is increased. The intensity is, however, very sensitive to changes in the amount of vapour present, and may be enormously increased, even at moderate temperatures, when a large amount of calcium is vaporised.

The H and K lines, however, are quite different in their behaviour. They do not appear in the electric furnace spectrum at temperatures below 2400°, and become stronger as the temperature is raised.

These results were obtained with a vacuum, and when hydrogen at atmospheric pressure was used it was found that the lower temperature limit at which these lines appeared was apparently raised. This very probably was due to the fact that the actual temperature of the vapour was lower owing to the convection set up by the hydrogen and the absence of oxidation. The previous result as to the strengthening of these lines by increase in temperature was confirmed. When the furnace chamber was filled with air the H and K lines were materially strengthened, and consequently it would seem that their intensity is enhanced by the chemical reactions which are taking place.

The marked difference in the intensities of these lines and their behaviour as to reversal in the arc and furnace spectra does not seem capable of explanation purely by the difference in temperature between the two. It would seem necessary to assume that some other influence operates in the former in order to explain their very great intensity, and in view of the results obtained with the furnace chamber filled with air this added influence may well be chemical reaction.

In general, the increase in the intensity of these lines with tem-

[1] *Astrophys. Journ.*, **28**, 389 (1908); **29**, 381 (1909).

perature tends to confirm the view that they are spark or enhanced lines,[1] for their behaviour in that respect is analogous to such typical enhanced lines as $\lambda = 4481$ of magnesium, $\lambda = 5339$ and 5379 of cadmium, etc., which show similar increase in intensity with rise in temperature. On the other hand, the range of temperature of the H and K lines extends much lower than is usual with enhanced lines.

In later papers King gives his temperature classification of the lines of calcium, strontium, barium and magnesium,[2] but for the moment a description of this classification may be postponed.

The production of the enhanced lines in the electric furnace spectrum was studied by King with very interesting results in the case of titanium, and as a new phenomenon was observed in the operation of the furnace we may consider this investigation in some detail.[3] In some earlier work on the electric furnace spectrum of titanium it was found that none of the enhanced lines made their appearance. On the other hand, these lines are present in the arc spectrum of this element, and consequently it seemed probable that they would appear in the furnace spectrum if a sufficiently high temperature could be reached. From previous experience it was known that very high temperatures introduced a certain amount of continuous spectrum, which was sufficiently strong to mask faint lines with the moderate dispersion then employed. A more powerful spectrograph was now employed, giving with the second order from a plane grating a linear dispersion on the photographic plate of 0·9 A. per mm. in the region $\lambda = 4600$-4220, which was chosen for the present investigation, there being 40 enhanced lines of various intensities within those limits.

In the present investigation no jacketing material was used round the resistance tube, and with 30 volts 1600 amperes, falling to 1500, passed through the tube walls. The pyrometer readings gave temperatures of over 2600°, but the actual temperatures were probably higher, since the observations were made with open tubes. Under these conditions all the stronger enhanced lines appeared along with the arc lines.

In order to observe still higher temperatures rather stouter graphite tubes were taken and turned down until the thickness of the walls was reduced to about 2 mm. for a length of 5 cm. in the central portion. These tubes were capable of standing a current of 1400 amperes at 25 volts for several minutes, a rich titanium spectrum, including the enhanced lines, being obtained. When the potential difference was increased to 30 volts, the current rose to 1600 amperes and then commenced to drop, there being visible evidence of a rapid volatilisation of carbon. When the current reached 1500 amperes, a rapid

[1] By a "spark" or "enhanced" line is meant a line which is strong in the spark spectrum of an element, and either weak in the arc spectrum or entirely absent (see p. 83).

[2] *Astrophys. Journ.*, **29**, 190 (1909); **48**, 13 (1918); **51**, 179 (1920).

[3] *Ibid*, **37**, 119 (1913).

fall took place, showing that the tube was giving way with the formation of an arc. This arc lasted for about 5 seconds with 800 amperes passing before the ends of the tube became so far burned away that the arc broke. During this time the potential difference across the arc was only about 30 volts. When the furnace was opened after cooling it was found that there was a cylindrical gap of from 3 to 4 mm. in the tube.

King succeeded in photographing the spectrum immediately before and after the arc was formed, and the results are of great interest. The higher temperature conditions existing before the arc is formed certainly favour the formation of the enhanced lines, for these are visible with great intensity. The conditions after the rupture, when there has been established what we may call the tube arc, are particularly favourable for these lines. A consideration of these conditions shows that they differ materially from those normally present in the furnace arc or spark as usually operated. Possibly they approach those of solar and stellar atmospheres more nearly than in any of our laboratory sources. When the tube has broken, the vapour at a very high temperature is surrounded by an arc which consumes nearly 24 kilowatts, this being of a different order from the 500 watts of an ordinary laboratory arc. Then, again, it must be remembered that the potential difference across the arc is not greater than 35 volts. Perhaps the most striking result is shown by a photograph of the spectrum taken some seconds after the tube gave way, thus eliminating any possibility of an effect due to a sudden and momentary change when the arc was formed. This photograph showed all the enhanced lines and very little besides.

In order to test whether there was any difference in the spectrum of the vapour at the centre of the tube and that near the wall where the arc was in action photographs were taken with a long slit. Before the tube had given way there was no perceptible difference in the strength or appearance of the lines from centre to wall. After the tube had given way and the arc had formed a very striking difference made its appearance. Whilst the arc lines were much weaker in the centre of the tube than near the wall, the enhanced lines showed little or no variation in intensity across the diameter of the tube. In other words, the enhanced lines were very strong in the middle of the tube relatively to the arc line. A further point of great interest is the presence of the enhanced line of carbon at $\lambda = 4267$, which is strong near the centre of the tube and scarcely visible near the walls of the tube.

Another remarkable phenomenon appears in the spectrum when the tube burns through. The ends of the long lines visible close to the walls show nearly constant intensity across their width, but on approaching the centre of the tube the red side of the lines becomes increasingly stronger. In the case of reversal the lack of symmetry is very marked. The enhanced lines of titanium do not show this effect, but this may be due to the fact that they are narrow and sharp,

since the enhanced line of carbon is very unsymmetrically reversed, the longer wave-length side being almost twice as intense as the shorter wave-length side. In all probability the effect is due to an unsymmetrical broadening of the lines, and at any rate it must very materially affect the wave-length measurements of the lines and must be recognised as a phenomenon likely to occur in any source in which the vapour exists in a state similar to that in the present experiments.

It is important to note that the wave-length of lines, when measured in the spectrum given by the condensed spark, are often greater than when measured in the spectrum of the arc,[1] the result being that the condensed spark is useless as a source of standard wave-lengths. It is clear from the present results that these shifts in passing from arc to spark cannot be due to the pressure effect, as has been suggested.

The observations recorded in these experiments were confirmed in later work [2] with other elements, with, however, the added fact that the gradation of intensity across a diameter of the tube was not found to be the same for the enhanced lines of every element studied. A modification was introduced into these experiments in order to guard against the escape of the metallic vapour when the resistance tube burns through. This was effected by placing an outer tube of graphite round the thin portion of the resistance tube, there being a clearance of 5 mm. between the two. This arrangement was found to be very successful in the case of magnesium, a quantity of which was placed in the outer tube just below the place where the arc formed. With this arrangement the enhanced line of magnesium at $\lambda = 4481$ was obtained as the strongest line in that region of the spectrum. It may be noted that this line does not appear in the arc spectrum.

We may next discuss King's work on the temperature classification of spectrum lines, which he has been able to establish in the case of certain elements with his electric furnace. The first element which comes under our notice is iron, which is dealt with in two papers.[3]

In order to indicate the relative response to temperature of different lines as regards both the stage of initial appearance and the rate of increase of their intensity with rise of temperature King drew up six classes. In order to do this it was necessary to have a reference class which should contain a number of lines which are strong at all temperatures, and show about the same rate of intensity change. He called this group Class I. (B), and in the case of iron the lines of this class are plentiful throughout the spectrum, except in the orange and red, and the exposures were so adjusted that these lines had the same intensity in the photographed spectra for all the different temperatures employed.

Class I. (A) has the distinguishing characteristic of strong intensity at all furnace temperatures after radiation commences, and notable

[1] N. A. Kent, *Astrophys. Journ.*, **22**, 182 (1905).
[2] *Ibid.*, **38**, 315 (1913).
[3] *Ibid.*, **37**, 239 (1913); **56**, 318 (1922).

weakness in the arc spectrum. As compared with the reference Class I. (B), some of the lines of Class I. (A) show a slight decrease in intensity as the temperature rises, but they still remain among the stronger furnace lines at the highest temperatures. They are, however, weak in the arc, sometimes being barely visible in a normally exposed arc spectrum.

Some difficulty may arise from the fact that the lines due to impurities show a similar behaviour, the strongest lines of an impurity being often given with greater intensity in the furnace spectrum than in the arc spectrum of the same specimen of iron. King, in each case, used as comparison the arc spectrum of iron, and only classified those lines in the furnace spectrum which are accepted as being due to iron. Possibly, of course, a few of the Class I. (A) lines of iron may be due to impurities, no special investigation being undertaken to test this point, but their regular behaviour in both arc and spark is that of weak iron lines, so that the phenomena offered by this important class may be accepted as real with a high degree of probability.

Class I. (B) includes the well-known group of flame spectrum lines of iron which are readily given by the hotter flames and are relatively strong in the outer envelope of the arc. These lines are strong in the furnace spectrum at all temperatures. They usually have a moderate intensity in the arc spectrum, although those in the yellow-green region are among the strongest arc lines. There is usually a clear distinction in the arc spectrum between the lines of Class I. (B) and those of Class I. (A), the conditions prevailing in the arc being unfavourable for the appearance of the latter.

Class II. includes a large number of the stronger arc lines. The lines of this class are distinct, and often strong at the lowest temperatures, but as the temperature rises their intensity increases much faster than is the case with the lines of Class I. They are usually more intense in the arc than at the highest furnace temperatures.

Class III. These lines are absent or weak at the lowest temperatures, appear distinctly at medium temperatures, show a rapid increase in intensity with rise in temperature, and are strong in the arc. The rate of increase in intensity is the same as for the lines of Class II., but these lines require a higher temperature for their production.

Class IV. These lines appear only at the highest furnace temperatures (perhaps very faintly at medium temperatures), but show a fair intensity. As a rule their relative intensity in the arc is much greater than in the furnace spectrum.

Class V. These lines are absent from, or very faint in, the furnace spectrum, their intensity varying very greatly in the arc spectrum. It is possible to obtain many, if not all, of these lines in the furnace spectrum by long exposures at the highest temperatures, but the difference between their intensities in the furnace and arc spectra is greater than is the case for lines of Class IV.

King says that it is usually easy to assign a line to its class in the

above scheme. A few lines are on the border between Classes I. (A) and I. (B), since the distinction depends mainly on their intensity in the arc.

A decision between Classes IV. and V. is sometimes difficult for weak lines, but the difference for such lines is not important. The distinction is clear and valuable when we have a strong arc line which may be excited at the highest temperatures in the furnace readily (Class IV.) or only with great difficulty (Class V.).

In general, Classes I. (A), I. (B), and II. may be regarded as including low temperature lines, Class III. medium temperature, and Classes IV. and V. high temperature lines.

A very important point rises in connection with the observed intensities of furnace spectrum lines, namely the possibility that the intensity of a line belonging to the element under investigation may be enhanced by the presence of an impurity line having very nearly the same wave-length. In the case of iron the strongest lines of the following impurities were present, chromium, manganese, titanium, and vanadium, the two last being given by the Acheson graphite. In the present investigations the furnace spectra of these four elements were known, so that in the case of a suspected blend it was a simple matter to see whether a strong line occurred at that wave-length in one of the impurity spectra. The problem was also simplified by the classification of the lines of the impurity spectra. Thus, a low temperature iron line is blended with the chromium line at $\lambda = 5204{\cdot}680$. Now this line is one of those which are similarly affected by temperature in any source, and it becomes possible from an examination of the furnace spectrum of chromium to measure the intensity of this line with respect to the other two. In this way a correction can be applied to the intensity of the iron line. Care must be taken also to guard against errors being introduced by the blending of iron lines with the lines of the carbon band spectra which always appear at high temperatures.

It is not possible to quote the whole of King's table of furnace lines of iron and their classification, but Table III. contains all those observed by him between $\lambda = 5022{\cdot}439$ and $4745{\cdot}992$.

In his later work King discards the special sub-division of Class I. into A and B, according to the relative weakness of the lines in the arc, and uses the letter A for any line which shows relative weakness in the arc irrespective of the class to which it belongs.

In his second paper on the electric furnace spectrum of iron, King supplements very considerably the results given in the first paper, and part of this new work is very interesting in that he makes use of absorption methods for the classification of the lines in the ultra-violet region. The emission spectrum given at a particular temperature of the furnace stops at a point in the ultra-violet which is somewhat short of the limit of the continuous spectrum given by a black body at that same temperature. There is thus set a limit beyond which it is not possible to extend the furnace emission spectrum

TABLE III.

λ (Rowland.)	Intensities.				Class.	Remarks.
	Arc.	Furnace.				
		High temp.	Medium temp	Low temp.		
5202·439	8	4	1	—	IV.	——
5198·888	4	2	—	—	IV.	——
5195·113	10	9	5	2	I. (B)	——
5192·523	30	5	Tr.	—	IV.	——
5191·629	20	4	—	—	IV.	——
5171·778	20	10	6	3	II.	——
5169·069	4	8	8	10	I. (A)	——
5167·678	40	12	9	7	II.	——
5166·454	4	8	8	10	I. (A)	Blend with weak Cr line, which probably has little effect.
5162·449	10*n*	?	—	—	IV. ?	Blend with C at high temperature. Probably present but weak.
5152·087	4	6 ?	3	1	I. (B)	Blend with C at high temperature.
5151·020	6	5	4	2	I. (B)	——
5143·111	6	5	4	3	I. (B)	——
5139·644	20	4 ?	Tr.	—	IV.	Blend with C at high temperature.
5139·427	10	4 ?	—	—	IV.	Blend with C at high temperature.
5137·558	6*n*	—	—	—	V.	——
5133·870	20*n*	?	—	—	V.	Blend with C. Very weak if present.
5127·533	5	8 ?	4	2	I (B)	Blend with C at high temperature.
5125·300	6*n*	—	—	—	V.	——
5123·899	6	9 ?	5	3	I. (B)	Blend with C at high temperature.
5110·574	10	8 ?	10	15	I. (B)	Remarkably strong at low temperatures. Blend with C at high temperature.
5107·823	8	3	2	1	II.	Blend on some plates makes estimates difficult.
5107·619	6	4	3	2	I. (B)	——.
5098·885	8	4	Tr.	—	IV.	——
5083·518	7	10 ?	7	4	I. (B)	Blend with C at high temperature.
5079·921	4	6 ?	4	2	I. (B)	Blend with C at high temperature.
5079·409	6	3	Tr.	—	IV.	——
5074·932	10*n*	—	—	—	V.	——
5068·944	10	—	—	—	V.	——
5065·207	6*n*	?	—	—	V.	Concealed by C if present.
5051·825	10	10	8	6	I. (B)	——
5050·008	15	12	2	—	III.	——

TABLE III (*Continued*).

λ (Rowland.)	Intensities.				Class.	Remarks.
	Arc.	Furnace.				
		High temp.	Medium temp.	Low temp.		
5041·936	10	7	4	1	III.	Blend with Ca; probably has little effect on furnace intensity.
5041·255	7	7	6	3	I. (B)	—
5028·308	4	—	—	—	V.	—
5027·305	5*n*	—	—	—	V.	—
5022·414	6	—	—	—	V.	—
5015·123	10	—	—	—	V.	—
5012·252	12	10	9	8	I. (B)	—
5006·306	20	4	1	—	III.	—
5005·896	10	—	—	—	V.	—
5002·044	12	1	—	—	V.	—
4994·316	8	9	9	4	I. (B)	—
4985·730	7	1	—	—	V.	—
4985·432	7	Tr.	—	—	V.	—
4984·028	6*n*	—	—	—	V.	—
4983·433	5*n*	—	—	—	V.	—
4982·682	8*n*	—	—	—	V.	—
4978·785	2	—	—	—	V.	—
4973·281	3	—	—	—	V.	—
4966·270	8	1	—	—	V.	—
4957·785	60	12	6	1	III.	—
4957·480	20	5	2	—	III.	—
4946·568	4	5	—	—	IV.	—
4949·868	4	10	8	5	I. (B)	—
4938·997	10	3	—	—	IV.	—
4924·956	3	—	—	—	V.	—
4920·685	60	12	4	Tr.	III.	—
4919·174	30	8	2	—	III.	—
4903·502	12	4	1	—	III.	—
4891·683	50	12	3	—	III.	—
4890·948	25	8	2	—	III.	—
4885·620	2	—	—	—	V.	—
4878·407	12	5	2	—	III.	—
4872·332	20	7	2	—	III.	—
4871·512	25	9	3	—	III.	Furnace line may be slightly affected by V. blend.
4859·928	15	6	2	—	III.	—
4789·849	7	—	—	—	V.	—
4787·003	5	1	—	—	IV.?	Furnace line may be V.
4773·007	3	3	2	—	III.	—
4768·595	3*n*	—	—	—	V.	—
4745·992	3*n*	—	—	—	V.	—

towards the ultra-violet. It was found, however, that iron vapour selectively absorbs rays of shorter wave-length than it is able to emit, and by the use of white light from a very hot source it was found possible to observe absorption lines to as far as $\lambda = 2298$ in the case of iron vapour at 1600°, when the emission spectrum ceases at $\lambda = 3440$. Since there seems no reason why lines observed in this way should not be classed as low temperature lines, it was considered by King to be legitimate to use this method of arranging the lines in high and low temperature classes.

As the source of white light for the absorption spectra observations, three methods may be employed. A graphite plug in the centre of the resistance tube can be used, and the results obtained by this method will be discussed below. The most satisfactory source is a 900-watt nitrogen-filled lamp, operated with 30 amperes and provided with a quartz window. The third method is to use the light from exploded wires of aluminium or lead,[1] and this gives very admirable results, but the method has the inconvenience of the presence of the absorption lines of the metal used and of the very large number of separate explosions necessary to produce sufficient effect on the photographic plate with a spectrograph of high dispersion.

In this more recent work on iron King used three temperatures, namely :—

Low temperatures . .	1600°-1700°
Medium temperatures . .	2000°
High temperatures . .	2500°-2600°

He gives in his tables the classification of 904 iron lines between $\lambda = 3878$ and $\lambda = 2298$. In view of the lower temperature limit now employed, he gives a revised classification of 262 lines between $\lambda = 4531$ and $\lambda = 3884$, which has involved, as may at once be understood, the raising of the class of some of the lines previously assigned to Class I.

By prolonged exposure with a grating of 1 metre focal length King succeeded in recording 11 lines emitted at 1400°. These lines, therefore, are the most persistent low temperature lines of iron, and their wave-lengths and furnace intensities are given in Table IV.

As will be shown in Volume III., Chapter I., in connection with spectral series phenomena, Fraülein Gieseler and Dr. Grotrian measured the absorption spectrum of iron at 1250°, and within the region covered by the Table IV. found the lines $\lambda = 3886{\cdot}29$, $3859{\cdot}91$, $3745{\cdot}56$, the strongest line being $\lambda = 3859{\cdot}91$.

In addition to his work on the iron spectrum, King has also classified the lines of titanium,[2] vanadium,[3] chromium,[4] cobalt,[4] nickel,[4] manganese,[5] and scandium.[6] These observations call for little comment apart from an indication of their great value. As will be

[1] Anderson, *Astrophys. Journ.*, **51**, 37 (1920). See p. 86.
[2] *Ibid.*, **39**, 139 (1914); **59**, 155 (1924).
[3] *Ibid.*, **41**, 86 (1915); **60**, 282 (1924).
[4] *Ibid.*, **42**, 344 (1915).
[5] *Ibid.*, **53**, 133 (1921).
[6] *Ibid.*, **54**, 28 (1921).

TABLE IV.

λ in I. (A).	Int.	λ in I. (A).	Int.
4482·18	2	3899·70	5
4461·65	4	3895·65	5
4427·31	8	3886·29	6
4383·55	Trace	3878·58	5
4375·93	10	3859·91	4
4216·18	2	3856·37	4
3930·30	8	3825·89	1
3927·94	8	3824·44	2
3922·92	8	3820·43	1
3920·26	8	3745·56	1
3906·47	2	—	--

readily understood, the temperature limits adopted are not necessarily the same for each element studied, and more particularly is this true for the low temperature limit, since this is determined by the temperature at which radiation commences. The three temperatures chosen are shown in Table V. :—

TABLE V.

Titanium.	Vanadium, Chromium, Cobalt and Nickel.	Manganese.	Scandium.	
2000°	2000°-2150°	1700°	1900°-2000°	Low.
2250°	2300°-2350°	2000°	2250°	Medium.
2600°	2500°-2600°	2400°	2600°	High.

In the cases of chromium and manganese King gives lists of the lines which are exhibited at the lowest temperature, or what may be called the residual furnace lines. Table VI. contains the chromium lines which are radiated at a temperature of 1700°-1800°, together with their intensities at that temperature.

In Table VII. are given the manganese absorption lines which are given at a furnace temperature of 1560°.

In addition to this work on the temperature classification of spectrum lines, King also made certain other observations, two of which may be mentioned here. The consideration of his work on electric furnace spectra under pressure may be postponed.

The first piece of work coming under notice at this stage is an extension of the absorption spectra observations, and is of great interest.[1] Reference has already been made to one of the methods

[1] *Astrophys. Journ.*, **51**, 13 (1920).

TABLE VI.

λ.	Int.	λ.	Int.	λ.	Int.
6630·25	3	5022·04	Tr.	4339·90	20
6363·03	6	4965·10	6	4339·62	20
6330·30	12	4942·68	10	4337·74	30
5410·01	80	4652·38	50	4289·90*	150
5348·50	70	4651·49	40	4275·00*	175
5345·99	80	4646·35	60	4254·51*	200
5329·30	Tr.	4626·35	50	3941·67	12
5328·53	1	4616·28	50	3928·82	8
5300·89	20	4613·53	40	3921·21	8
5298·46	60	4600·90	50	3919·32	12
5296·86	60	4591·61	35	3916·41	6
5265·90	30	4580·26	50	3908·91	10
5264·35	50	4565·70	25	3903·29	10
5247·72	50	4546·10	60	3903·05	—
5208·60	100	4497·03	60	3894·20	6
5206·24	80	4412·44	4	3886·92	7
5204·71	70	4391·93	8	3885·36	7
5123·63	2	4385·15	40	3883·48	8
5122·27	1	4373·42	10	3732·19	3
5092·93	1	4371·48	50	3730·96	3
5073·10	5	4359·82	40	3615·77	1
5068·45	1	4351·98	30	3605·49*	20
5052·08	3	4351·22	20	3593·64*	20
5048·95	Tr.	4344·68	40	3578·81*	25

* These lines were also observed at 1250° by Fraülein Gieseler and Dr. Grotrian, as will be described in Volume III., Chapter I.

TABLE VII.

λ.	Int.	λ.	Int.
4823·71	10	4048·90	3
4783·62	10	4041·53	10
4754·24	10	4035·88	3
4083·82	2	4034·62	50 R
4083·11	2	4033·21	75 R
4079·61	—	4030·92	100 R
4079·38	3	4018·28	3
4063·70	1	3834·50	1
4059·09	1	3823·64	1
4055·70	1	3806·90	2

used by King in observation of absorption lines, namely, the use of a short graphite plug placed in the centre of the heated resistance tube. This arrangement gives a close approach to black body conditions.

In discussing the application of Kirchhoff's law to absorbing vapours, Kayser [1] points out that lines in one and the same spectrum

[1] *Handbuch der Spectroscopie*, II., 53.

may differ in their absorptive power, so that a given relation between the luminous background and the vapour will not necessarily reverse all the lines emitted by the vapour. If the emission at a given wave-length of the graphite plug, which is practically that of a black body, be e, and that of a black body having the same temperature as the vapour be e_1, then the emissive power of the vapour will be given by e_1A, where A is the absorption coefficient of the vapour for light of the given wave-length. The total emission of light of the given wave-length from the tube filled with vapour will be

$$e + e_1\mathrm{A} - e\mathrm{A} = e - (e - e_1)\mathrm{A}.$$

In order that an absorption line may appear, $(e - e_1)$A for that wave-length must be greater than a minimum positive value, the intensity of the line increasing as this value becomes greater. It is evident, therefore, that the emission of the vapour for that wave-length must be less than the emission of the graphite plug. If $e - e_1 = 0$, the continuous spectrum of the plug will only be visible. This condition King frequently obtained by locating the plug in a cooler part of the resistance tube, thereby reducing the value of e. In spite of the fact that the vapour may then strongly absorb the given wave-length, no trace of an absorption line will be seen because the large value of A is rendered ineffective by the zero value of $e - e_1$.

If there be a considerable difference between the emissive powers of the plug and the vapour, *i.e.* $e - e_1 > 0$, then the value of A will determine whether a line will appear as a strong absorption line or be invisible, because A is not very different from zero. As Kayser points out, the well-known difference in the reversibility of lines in the arc affords definite evidence that the value of A is not the same for all lines.

It is clear that the electric furnace can furnish data of value in this matter. Thus, a photograph of the spectrum emitted by the heated vapour will show two or more lines of the same intensity. If without altering the temperature the graphite plug be inserted in the resistance tube, then any real difference in the intensities of these lines now seen as absorption lines will establish a real difference in the absorptive power of the vapour for those wave-lengths.

The difference of temperature between the graphite plug and the vapour in the tube is not easy to determine. King found that the temperature of the plug varied remarkably little with its position, provided that it were not placed within about 1 inch from the supporting blocks. The total variation was of the order of 100° at 1800°, and not more than 25° at 2400°. How far the vapour takes up the temperature of the surrounding walls is not certain, but there can be no question but that with the plug in the centre of the tube the emissive power of the plug is greater than that of the vapour for all the wave-lengths dealt with, that is to say $e - e_1 > 0$.

Observations were carried out with iron, titanium, cobalt, nickel, calcium, and barium, and it was found at once that the absorption

spectra were very different from the emission spectra at the same temperature. For example, titanium showed no absorption lines at 2000°, although, as mentioned above, a considerable number are visible as emission lines at that temperature when the plug is absent. When the temperature of the plugged tube is raised to 2400°, those lines which are visible as emission lines at 2000° are now visible as absorption lines. These lines are low temperature lines of Classes I. and II. Similar results were obtained with the other metals mentioned above, and it follows that the absorption spectrum corresponds with the emission spectrum as observed at a temperature which is lower by several hundred degrees.

King observed a very decided difference in the absorptive power of a vapour for the lines of the different temperature classes. The greatest absorptive power, that is to say, the greatest value of A, is shown for the lines of Class I. The stronger lines of Class II. also appear as strong absorption lines, but there is a marked difference between the two classes. In the case of two lines, belonging to Classes I. and II. respectively, which have equal intensities in emission, the line of Class I. will be the stronger in absorption. Those lines of Class III. which appear faintly in the emission spectrum at lower temperatures can be observed in the absorption spectrum, though with some difficulty. As far as the blue and violet regions are concerned the absorption spectrum of iron at 2600° is very similar to the emission spectrum at 1650°, this being the lower limit for appearance of the Class III. lines. The lines of Class I. are the strongest in each, as necessarily follows from the fact that they are the low temperature lines and the fact that the absorptive power of the vapour is the greatest for these lines. At the higher temperature we know that Class II. and III. lines are being emitted, but the absorptive power of the vapour is weak, with the net result that they do not appear either as emission or absorption lines, or at any rate, with very feeble intensity. The same argument applies to the absence of the lines of groups IV. and V. from the absorption spectra. Owing to the small absorptive power of the vapour for the lines of these higher classes, a black body at a higher temperature is required to reveal them as absorption lines.

Perhaps the most interesting results recorded by King in this field are those obtained when the graphite plug is placed behind the centre of the resistance tube and there is an intervening layer of vapour at a higher temperature than the plug. Owing to the marked difference between the absorptive power of the vapour for lines of different classes the result is just what would have been anticipated. The low temperature lines appear as absorption lines and those of higher classes appear as emission lines. By moving the plug to a still cooler portion of the tube the intensity of the emission lines is increased, and a position can be found where all the lines appear as emission lines with the exception of those of Class A, which appear as absorption lines. It thus follows that it is merely a matter of adjusting the

intensity of the emission by the plug in order to obtain all the lines of the higher temperature classes as emission lines (including the enhanced lines, if present) and those of Class I. as absorption lines. This establishes the very definite difference in the absorptive power of the vapour for the lines of different classes.

Furthermore, by placing the graphite plug at a distance of 2 or 3 cm. from the farther end of the resistance tube its emissive power may be made approximately equal to that of the vapour in the centre of the tube. Under these conditions some lines appear as emission and some as absorption lines, whilst some lines do not appear at all, because the emissive power of the vapour for those lines is counterbalanced by its absorptive power. As an example of this calcium vapour can exhibit the H and K lines as emission lines, and the low temperature line $\lambda = 4227$ as an absorption line, no other line being visible between $\lambda = 5000$ and $\lambda = 3500$. In the case of iron a condition was obtained when the strongest lines in the blue region, $\lambda = 4384$, 4326, 4308, 4272, were entirely absent, whilst the majority of those in Classes II. and III., though of less intensity, appeared as emission lines, and many of those in Class I. appeared as absorption lines.

It is evident that it is possible by changing the emissive power of the plug to eliminate from the spectrum any set of lines for which the vapour has the same absorptive power. These results would seem to have a special significance with relation to the spectra of certain stars which contain both emission and absorption lines, and from which there are absent certain lines belonging to well-known series. King quite rightly points out that the phenomena that we have been considering are just those likely to be seen when masses of vapour with temperature gradients are under spectroscopic examination. This suggestion would seem to be particularly applicable to Novae, that is to say, new-born stars, where such conditions of steep temperature gradients most probably exist during the period of enhanced luminosity.

The problem of the absorption spectra of vapours was dealt with by King from a rather different point of view in a later paper.[1] This extended work was undertaken to test some of the theoretical views put forward by Saha,[2] the particular points investigated being (1) the conditions necessary to obtain any series type of line in absorption; (2) the effect on lines due to the ionised atom of the presence of other atoms with lower ionisation potentials; (3) the question as to whether under given conditions of the metallic vapour a line can be obtained as an absorption line at a lower temperature than it can be obtained as an emission line.

In order to understand the first two of these three points some knowledge of spectral series is required, and this section of our subject will be dealt with in Vol. III., Chapter I. A very brief indication

[1] *Astrophys. Journ.*, **55**, 411 (1922).

[2] *Phil. Mag.*, **40**, 472, 809 (1920); **41**, 267 (1921); *Proc. Roy. Soc.*, A, **99**, 135 (1921).

of the present-day knowledge will be sufficient to explain the problem King had in view in carrying out this work. In the first place, the lines in the spectra of the elements can be for the greater part grouped in series, each series consisting of a number of lines the wave-numbers of which can be expressed by a single formula involving some function of consecutive integral numbers. As an example of a series formula that suggested by Hicks may be instanced :—

$$\nu = \mathrm{K} - \frac{\mathrm{N}}{\left(n + \alpha + \frac{\beta}{n}\right)^2},$$

where K is a constant and denotes the upper limit of the series, α and β are constants, and $n = 2, 3, 4, 5$, etc. In the spectra of the alkali metals each series consists of doublets, whilst each series in the case of the alkaline earth metals consists of singlets or triplets. In each system, singlet, doublet, or triplet, there are four types of series, known as the principal, sharp, diffuse, and fundamental series, which are interconnected by certain simple relations. In these particular cases it is the principal series which exhibit themselves as absorption lines when the metallic vapours are examined in the ordinary way. A typical pair belonging to a principal series is shown by the two D lines of sodium.

According to the Bohr theory the excitation of the atom, whereby it evolves its characteristic spectrum lines, consists in the displacement of one or more electrons from their normal orbits to other orbits, and the return of these displaced electrons to their normal orbits is associated with the evolution of fixed and definite quantities of radiant energy which evidence themselves as spectrum lines. The displacement of an electron, that is to say, the reverse process to the emission of a line, requires the supply of an amount of energy which is exactly equal to the energy evolved in the emission of that spectrum line. This energy can be given to the atom by exposing it to the action of a stream of electrons travelling with a known velocity which is governed by a definite potential fall. The potential fall, which gives these electrons sufficient velocity to cause the ionisation of the atoms of the element under investigation, is known as the ionisation potential of that element, whilst the potential fall, which gives the free electrons sufficient velocity to cause the displacement of the atomic electrons from their normal orbits to another orbit within those atoms, is known as the resonance potential for the spectrum line radiated when the electrons return once again to the normal orbits. These ionisation and resonance potentials are measured in terms of volts. It must be remembered that there is a " normal " orbit for each of the principal, sharp, diffuse, and fundamental series.

It has already been pointed out that in the case of the alkali and alkaline earth metals the principal series only exhibit themselves as absorption lines under ordinary circumstances, and Saha's explanation of the absence of the sharp and diffuse series is that the temperature

is not sufficiently high, this being a fairly obvious deduction from the fact that these series require stronger excitation for their appearance in emission spectra. King's electric furnace apparatus offers a very simple method of testing this point. He found that in the case of sodium vapour at 2250° the following doublet lines were emitted, in addition to the D lines, which were strongly reversed :—

λ.	
5688·22 5682·68	Diffuse series.
6160·73 6154·21	Sharp series.
5153·65 5149·09	Sharp series.

This proves that the production of these two series was well within the range of the furnace. The second pair of the principal series is at $\lambda = 3302{\cdot}94$ and 3302·34, and was outside the range of spectrum dealt with.

The absorption spectrum was observed by the graphite plug method, and when the temperature of the plug was 2650°-2700° there were observed the following pairs :—

λ.		λ.	
5688·22 5682·68	Diffuse series.	6160·73 6154·21	Sharp series.
4982·86 4978·61	,, ,,	5153·65 5149·09	,, ,,
4668·60 4664·86	,, ,,	4751·89 4748·02	,, ,,

When the temperature of the plug was 2350° the last two pairs of the sharp series were not detected, this absence being probably due to the fact that those lines are extremely narrow at low temperatures of the furnace operated in a vacuum, with the result that the absorption lines were below the limit of photographic resolution. Apart from this, the sharp and diffuse series exhibit themselves with equal ease in absorption spectra.

Since similar results were obtained with potassium, rubidium, and cæsium, it may be concluded that the subordinate series (sharp and diffuse) can be obtained in absorption spectra observations.

The second point investigated by King was the influence on the formation of the enhanced lines of a metal of the admixture of a second metal with a lower ionisation potential. Since we know that the enhanced lines are due to an ionised atom, Saha suggested that in a vapour which is exhibiting both arc and enhanced lines there exists an equilibrium condition represented by

$$M \rightleftarrows M^{+} + e$$

where M^+ represents the singly-ionised atom of the metal M and *e* the electron. If there be mixed with the vapour of M the vapour of a second metal, the ionisation potential of which is smaller than that of M, there will be formed an increased concentration of free electrons. By the law of mass action this should tend to set back the ionisation of M, with the result that there will be a smaller concentration of M^+ and a smaller intensity of the enhanced lines of M. The electric furnace gives an excellent opportunity of putting this to the test.

It may be mentioned that from previous experience it was known that so far as the arc lines of elements are concerned there is no evidence of any mutual influence when mixed vapours radiate their spectrum lines in the electric furnace, each vapour giving its own spectrum as if it were alone. In testing the effect of mixing two vapours on the enhanced lines King first examined a mixture of calcium and potassium, the ionisation potentials of which are 6·08 and 4·32 volts, respectively. The temperature chosen was 1800°, at which the enhanced lines K and H exhibit themselves distinctly, the intensities being sufficiently small to indicate any effect due to the admixed potassium. In the first experiments absorption spectra methods were employed, since the exposures are short and consequently there is little danger of change in the vapour in the resistance tube. The graphite plug was not used, but a beam of light from a powerful tungsten filament lamp was passed through the vapour, thereby securing absorption by the hottest portion of the vapour. In the first instance the absorption spectrum of calcium vapour only at 1800° was photographed, and the H and K lines appeared as absorption lines of moderate intensity, comparable with some of the lines in the group near $\lambda = 4300$ and the diffuse triplet at $\lambda = 4456$ to 4425, due to the neutral atom. The furnace was then charged with a mixture of calcium and potassium chloride, and then it was found that the H and K lines were hardly visible at all, the comparison lines of the neutral atom being of practically the same intensity as in the case of calcium vapour alone. It was noted that the line at $\lambda = 4227$ had very nearly the same width in the two photographs, which proves that the density of the calcium vapour was very nearly the same in the two cases. The experiment was repeated with calcium alone and with calcium and potassium, when once again the H and K lines were selectively much reduced in intensity by the presence of potassium.

The same results were obtained when the emission spectra of pure calcium and mixtures were compared. In this case cæsium chloride was used as well as potassium chloride, and found to give a greater effect, as would be expected from the fact that its ionisation potential of 3·81 volts is lower than that of potassium. This increased effect, however, may possibly have been due to the fact that the effective density of the cæsium was greater than that of the potassium. These results were fully confirmed by analogous observations with strontium and barium. Further confirmation of this effect was found later in

the suppression of the enhanced lines of titanium by the admixture of potassium.[1]

We may now deal with the third question investigated by King, namely, whether a line or group of lines can appear as absorption lines at a lower temperature than that at which they first appear as emission lines. Saha argued that a vapour at a temperature too low to radiate any lines should be able to absorb radiations which belong to the principal series (in the case of the metals of the alkali and alkaline earths). An increase in temperature should produce a stage at which the lines of the principal series are emitted and those of the sharp and diffuse series absorbed and not emitted. King only dealt with the existence of the first stage at which the lines of the principal series are absorbed and not emitted. The lines selected for the investigation were the following :—

Calcium . . .	$\lambda = 4226{\cdot}73$
Strontium . . .	$\lambda = 4607{\cdot}34$
Barium . . .	$\lambda = 5535{\cdot}53$

all three lines being the first members of the principal series of singlets. The metallic vapours were maintained at a constant temperature, and the emission and absorption spectra were photographed consecutively, the latter being observed with the light from the tungsten filament lamp. It must, of course, be remembered that the exposures necessary for the emission spectra are much longer than are sufficient for the absorption spectra, being two hours as compared with one-half to one minute. Absorption spectra photographs were taken both before and after the emission spectra photographs.

At a temperature of 1275° the calcium line $\lambda = 4227$ appeared as a strong absorption line, both before and after a two-hours period, during which the emission spectrum was photographed, but no trace of the line was obtained in the latter. In the case of strontium, the line $\lambda = 4607$ was observed as a very faint emission line at 1275°, but it vanished when the temperature was lowered to 1200°, at which it was clearly seen as an absorption line. Similarly with barium, the line at $\lambda = 5535$ showed very faintly in the photograph of the emission spectrum at 1500°, but no trace of it could be seen at 1400°, although at this temperature it appeared as a strong absorption line.

This account of King's work may be concluded with a short reference to his paper on the production of certain band spectra in the electric furnace.[2] The origin and structure of these spectra will be discussed in Vol. III., where it will be shown that they are specifically associated with radiation of energy by molecules as against line series, which are specifically associated with atomic phenomena. Three of these were investigated by King, namely, the bands given by titanium oxide, magnesium hydride and calcium hydride. The previous evidence as to the origin of these banded spectra was strongly

[1] *Astrophys. Journ.*, **59**, 155 (1924).

[2] *Ibid.*, **43**, 341 (1916).

in favour of the molecular compounds as their source and, as will be shown, this evidence is fully confirmed by King's experiments.

The first groups of bands, attributed to titanium oxide, have been investigated by Fowler,[1] who gave them the name of Antarian bands because they appear in the spectra of the stars of the third type, of which Antares is a typical member. In his work on the electric furnace spectrum of titanium, King found that there was no appearance of these bands when the furnace was operated in a vacuum. Again, no evidence of them was obtained when the furnace was full of air. On the other hand, when a stream of oxygen was introduced into the heated resistance tube containing titanium vapour the bands were developed very strongly. The temperatures used were 2300° and 2600°, and under these conditions the line spectrum of titanium was almost entirely suppressed. In other experiments the furnace was filled with pure oxygen, and then it was found that the spectrum could be changed at will from band and line spectra superposed to a pure band spectrum by increasing the supply of oxygen. Since there was no difference of temperature between the two conditions, it would seem to be proved that the bands have their origin in the oxide molecule, the disappearance of the line spectrum being incapable of any other explanation than the oxidation of the metallic vapour.

The magnesium hydride bands were also investigated by Fowler,[2] who concluded that they are only given in the presence of hydrogen, and, therefore, due to a compound of magnesium and hydrogen. King, in a similar way to that described for the titanium bands, was able to demonstrate that they were only given in the presence of hydrogen, though quite small quantities of hydrogen, such as are evolved by the graphite on heating, are sometimes sufficient for their production. He also found that a high temperature is unfavourable, and that if they appeared at 2500° it was usually as absorption bands. By passing a stream of hydrogen into a heated resistance tube at 2200° this spectrum was obtained very satisfactorily as emission bands.

The calcium bands were observed by Olmsted [3] in the spectrum of a calcium arc in an atmosphere of hydrogen. King observed that the same bands are emitted very strongly when a stream of hydrogen was passed into the resistance tube containing calcium vapour at 1900° to 2200°. Higher temperatures are not so favourable to their formation, although they were observed at times with temperatures as high as 2500°.

Explosion of Wires.—Reference was made above, on p. 76, to the use of the explosion of metallic wires as a powerful source of light in observations of the absorption spectra of metallic vapours. Since this method of illumination is one of high temperature, it may be considered at this stage. It consists in the passage of a very heavy current obtained by the discharge of a very large condenser through

[1] *Proc. Roy. Soc.*, A, **79**, 509 (1907). [2] *Phil. Trans.*, A, **209**, 447 (1909).
[3] *Astrophys. Journ.*, **27**, 66 (1908).

a fine metallic wire, and the experimental technique was first described by Anderson.[1]

The condenser consists of 98 plates of single-strength window glass 40 × 50 cm., having tin-foil coatings 35 × 43 cm. attached with shellac. The condenser is charged by a 500-watt, 26000-volt transformer through a mechanical rectifier, the arrangement being shown in Fig. 31. The entire circuit CSW is made as short and compact as possible in order to keep the inductance low and the frequency high. When the gap W is closed by a heavy conductor and the spark-gap S is about 2 mm., sparks pass at the rate of 2 or 3 per second; when the S is 2 cm., the sparks pass at the rate of one every two seconds. These sparks are very noisy, and it is necessary that the ears be protected when the observer is close to them. This is especially necessary when a wire is exploded in the circuit. With this apparatus it is not pos-

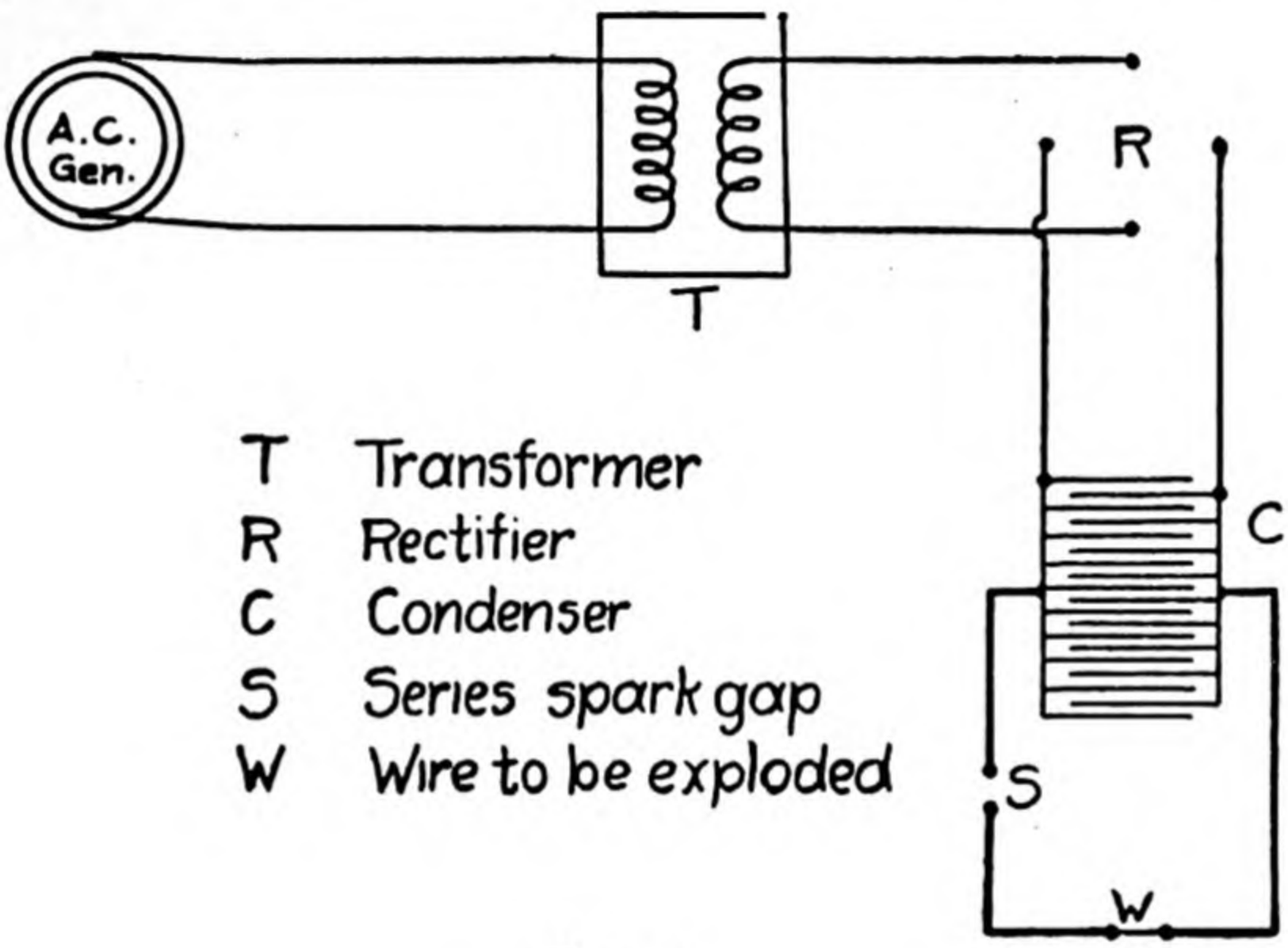


FIG. 31.

sible to obtain good effects with wires larger than No. 36 gauge (0·127 mm.) or longer than 8 cm., the most suitable length being 5 cm.

Anderson found that the best method is to place the wire in a groove 2·5 cm. deep and 3 mm. wide cut in a block of wood 4 cm. long, the explosion being viewed end on. At atmospheric pressure the spectrum obtained is perfectly continuous from above $\lambda = 5700$ to $\lambda = 2250$, with only absorption lines due to the particular metal composing the wire. When the wire was exploded under an exhausted bell jar Anderson investigated the region between $\lambda = 4200$ to $\lambda = 3600$, and found that at a pressure of 2 cm. all the lines were bright, with very few self-reversals. As the pressure of air is raised from 5 cm. to 13 cm. the continuous background increases rapidly in intensity, the reversals gradually becoming more prominent. At pressures of 15 to

[1] *Astrophys. Journ.*, **51**, 37 (1920).

20 cm. no bright lines are visible, the spectrum being perfectly continuous with the absorption lines very fine. Wires were used of nickel, iron, manganese, and copper, and the brightness of the continuous spectrum used with these metals falls in the order given.

This method of explosions of thin wires has been developed by Sawyer and Becker,[1] who substituted for the wire a fine fibre of asbestos, which is saturated with the solution of a soluble salt of the metal. They show that when the condenser is discharged through the solution on the fibres, the latter are not destroyed, and can be again moistened and the discharge again passed. Certain modifications were introduced in Anderson's design of apparatus, giving greater convenience in working and also greater efficiency. The condensers were made of sheets of roofing tin 8 × 10 inches placed between sheets of double strength window glass 10 × 12·5 inches. Each condenser consisted of sixteen tin sheets, and thc pile was firmly bound with cord, and a battery of sixteen such condensers was used. The condensers were placed in pairs in large glass accumulator jars and covered with transil oil. The total capacity was of the order of 0·3 microfarad. The charging voltage was obtained from a 50,000-volt 1-kilowatt transformer fed with 110-volt alternating current, rectification being obtained by means of a 100,000-volt 100-milliampere kenotron.

The chlorides were used of magnesium, calcium, strontium, and barium, and the spectrum only showed the lines of the metal and no lines of chlorine, hydrogen, or oxygen. A considerable number of lines due to various impurities were consistently present, notably those due to copper and zinc, which undoubtedly arose from the brass clamps holding the fibre. A striking fact is that the spectrum of the salt of any one of the above metals always showed many of the strong lines of the other three and also of cadmium. Although no great effort was made to secure purity of the salts used, the other metals could only have been present in very minute quantities. The results indicate that this method of excitation is capable of producing the spectra of substances which are present in very small concentrations. Certain lines were observed which could not be identified.

The range of spectrum investigated was $\lambda = 4550$-2280, and this was done for calcium, whereas in the case of strontium the region $\lambda = 4550$-3381, and in the case of magnesium and barium the region $\lambda = 3890$-3381 were omitted. Although a spectrograph was used of small dispersion (9·4 A. per mm.), the results obtained arouse considerable interest, since the lines observed belong to the doublet series of the ionised elements, only one single arc line appearing in the case of magnesium and calcium. The corresponding single lines of strontium and barium are in regions not investigated by these authors. It therefore would seem that the state of ionisation, that is the relative number of atoms ionised, is abnormally high, since it is well known that enhanced and arc lines are always seen together,

[1] *Astrophys. Journ.*, **57**, 98 (1923).

even in the spectra given by the most powerful sparks. Now it is known that the single lines mentioned which are—

	λ
Magnesium . . .	2852·13
Calcium . . .	4226·72
Strontium . . .	4607·34
Barium . . .	5535·69

are the last lines to disappear as the neutral atoms are progressively ionised,[1] their complete disappearance being an indication of complete ionisation. The ratio of the intensity of this singlet line to the intensity of the strongest doublet of the ionised atom affords a measure of the degree of ionisation. Sawyer and Becker give these ratios for calcium and magnesium, and these are quoted in Tables VIII. and IX.

TABLE VIII.

MAGNESIUM.

	Intensity of Doublet. λ = 2802·69 2795·53.	Intensity of λ = 2852·13	Ratio of Intensities.
King's electric furnace . . .	—	1200	—
Crew and McCauley, arc . . .	8	10	0·8
Eder and Valenta, spark . . .	10	8	1·2
Fowler, vacuum arc . . .	50	30	1·7
Exploded wire	10	2	5·0
,, solution	10	1	10·0

TABLE IX.

CALCIUM.

	Intensity of Doublet. λ = 3968·48 3933·67.	Intensity of λ = 4226·72.	Ratios of Intensities.
King, electric furnace . . .	55	1000	0·05
Crew and McCauley, arc . . .	400	500	0·8
Lockyer, spark	500	400	1·2
Loving, vacuum arc . . .	20	8	2·5
Exploded wire	10	2	5·0
,, solution	25	3	8·3
Solar chromosphere . . .	72	8	9·0
Stars of Class B	7	1	7·0

It will be seen that the degree of ionisation given by the exploded solution method is comparable with that in the sun and in the stars of Class B.

[1] The series designation of these lines is 1S – 2P (see Vol. III., Chapter I.).

Arc Spectra.—The second of the typical methods of excitation of substances is by means of the electric arc, and here we undoubtedly bring a higher temperature to bear than in the case of flames, with the result that the arc spectrum of an element is, in general, much richer in lines than is the flame spectrum. For the maintenance of an arc a direct current of 110 or 220 volts is preferable, and in cases where the substance to be examined is a good conductor and has not too low a melting-point, the method presents no difficulty. The simplest case is that of metals such as iron, copper, silver, etc., where two rods of the substance required are connected to the current mains, a resistance being placed in the circuit so that the current, which passes after the arc has been struck, is maintained at from 3 to 5 amperes. The striking of the arc is effected by bringing the two poles into contact, or by means of a rod of iron which is rubbed against the poles. The latter method is necessary when the poles, owing to previous use, have become coated with non-conducting oxide.

The electric arc is used in spectroscopy for two purposes. In the first place, it may be employed as a convenient source of light in a certain class of work on absorption spectra where a source of light is required which radiates as complex a line spectrum as possible. In the second place, it serves as an extremely convenient method of illumination when wave-length measurements are required. We may consider these two applications separately, since the requirements are quite different in the two cases, and the former may be considered first.

The arc between carbon poles is occasionally used as a source of light, the spectrum from the incandescent positive pole being almost continuous. This spectrum, however, does not extend very far into the ultra-violet. With this arc either an automatic feed may be used or a simple hand-feed instrument. In the former the two carbon poles are kept in contact when the current is not passing, and on starting the current they are separated by the action of an electro-magnet, and keep at a distance from one another depending on the strength of the current. As, however, it is generally necessary to maintain an image of the positive pole in a constant position, it will, as a rule, be found more satisfactory to use some hand-feed arrangement. All that is required is that each carbon pole be independently adjusted by means of a rack and pinion arrangement. This naturally requires attention from time to time, as the carbon poles burn away during the discharge. It will probably be found that in spite of the inconvenience of repeated attention the simpler arrangement proves more satisfactory.

In the use of the carbon arc for absorption work some trouble will be met with owing to the banded spectra given by the arc itself. Two banded spectra are present, namely, the Swan spectrum, which is probably due to carbon monoxide, and the so-called cyanogen spectrum, which is always visible when the electric discharge is passed between carbon poles in the presence of nitrogen. The complex fine-

line structure of these bands may be troublesome in observing fine-line absorption spectra, but comparison photographs taken of the arc with and without the absorbing layer will at once render the identification of the band lines possible.

In the case of a metallic arc, such as that between iron poles, I have found it very convenient to use a horizontal arc with the poles rotated in opposite directions, when long exposures are required. The apparatus is shown in Fig. 32, where A is a heavy wooden base to which are fastened two vertical brass uprights B, B, about 1¼ inches square and 10 inches high. C, C are two brass bearings which are firmly fixed in the uprights, and are bored out so that the steel tubes D, D work smoothly and truly in them. These steel tubes carry the

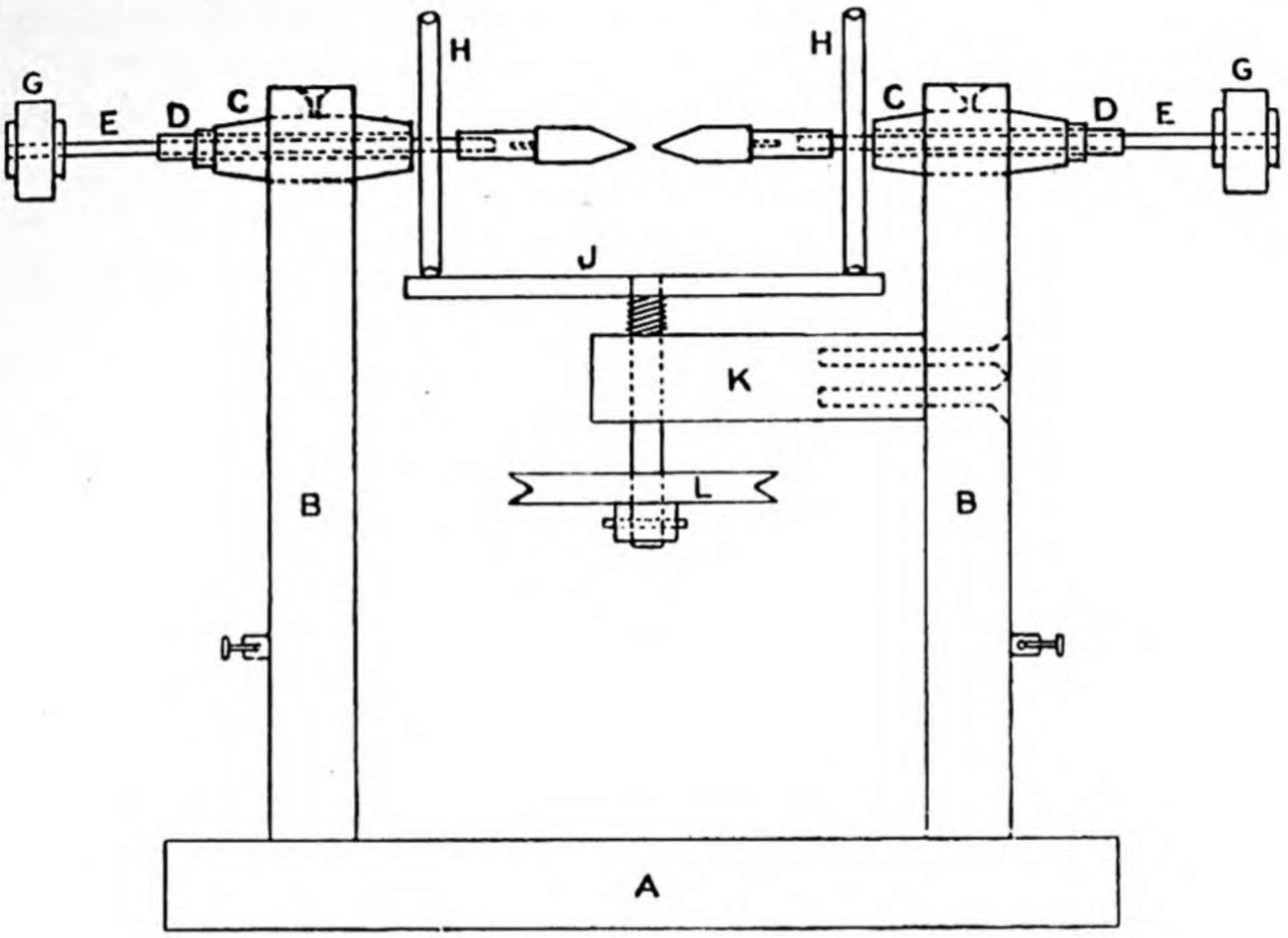


FIG. 32.

steel rods E, E, which fit rather tightly, so that when the steel tubes are rotated these rods turn with them. On these rods are mounted the pole-pieces, and the distance between these can at any time be regulated by moving the rods through the steel tubes. G, G are two discs of vulcanite which enable this to be done when the machine is in use. The rotation in opposite directions is provided for by the two vulcanised fibre friction wheels H, H, which are mounted on the steel tubes D, D. Around the periphery of each wheel is stretched a small rubber ring, a small groove having been turned in the periphery to keep the ring in position. These two wheels, or rather the rubber rings, press up against the brass disc J, which is carried by the horizontal support K. The machine is driven by an electric motor, which is connected by a cord to the driving wheel L. In order to keep the

brass disc up against the friction wheels, a small steel spring is put round the axle between the disc J and the horizontal support K.

This instrument works admirably, the speed of rotation being fairly high, 300 to 400 revolutions per minute; a perfectly steady arc is obtained with a current of about 4 amperes. Any suitable metal can, if desired, be used for the pole pieces, such as iron, one of the high speed steel alloys, copper, etc.

When the arc is to be used as a source of lines for very accurate wave-length measurements, recent work has shown that considerable errors are very liable to be introduced unless certain precautions are taken. For metallic arc spectra there is no question but that the most suitable form of arc is that devised by Pfund,[1] and the construction is shown in Fig. 33. This arrangement was first used as a source of iron lines, and in this case the lower (positive) electrode *a*, consisting of a rod of iron about 12 mm. in diameter, carries a bead of iron oxide *b* in a small cup-shaped bowl. The upper electrode *c* is an iron rod about 6 mm. in diameter, and projects about 3 mm. below a brass bush *d*, which is held in position by the set screw *e*. This serves to prevent the electrode from becoming too hot. The arc burns well with a direct current of about 3·5 amperes at 220 volts. After the electrodes have been carefully centred, the arc can usually be started by bringing the two electrodes into contact and then separating them. If this fails, contact may be established by means of a carbon rod or, alternatively, the bead of oxide may be heated to redness by means of a Bunsen burner, and then the two poles may be brought into contact. After the arc has been maintained for an hour or more, the upper electrode becomes coated with an incrustation of iron oxide. This should be removed and the brass bush readjusted before attempts are made to start the arc anew.

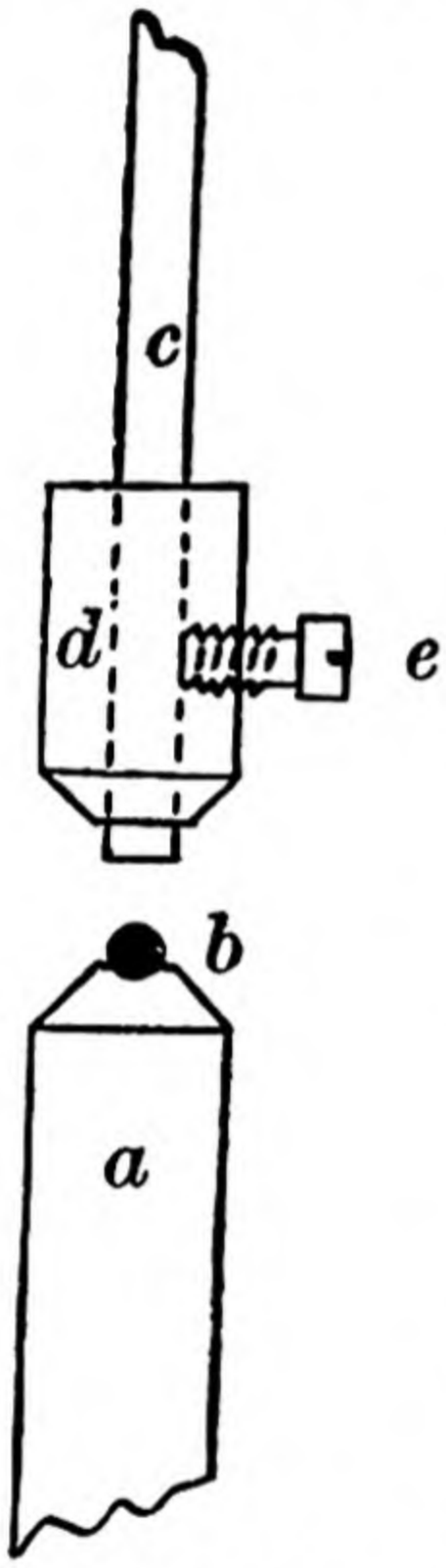


FIG. 33.

When the spectra of metals other than iron are under investigation the upper iron pole is replaced by a carbon rod about 1 cm. in diameter, the lower iron electrode being as before. The bead of iron oxide is replaced by a bead of the required metal or its oxide. Such a bead is readily made by placing a small piece of the metal in question in the cup of the lower electrode. When the arc is started the bead is formed immediately, and if it is found to be too small, its size can be increased by feeding it with wire of small fragments of the same metal, while the arc is burning. The bead should be about 3 mm. in diameter, and the essential condition for the proper behaviour of the arc is that the bead of molten metal or oxide be in the spheroidal

[1] *Astrophys. Journ.*, **27**, 296 (1908).

state and that it has a larger diameter than the cup in which it rests, as shown in Fig. 33.

There is no difficulty in preparing beads of the different metals or their oxides, and all that is necessary to change from, say, the copper arc to the nickel arc is to remove the copper bead by a pair of tweezers and to replace it by a nickel bead.

Of the various metals experimented with by Pfund, namely, iron, nickel, cobalt, copper, silver, and platinum, the only one which at first gave some trouble was silver. With the 12 mm. iron rod the silver bead failed to melt and the arc was, in consequence, unsteady. The difficulty was surmounted by using an iron rod which was only 7 mm. in diameter. In the case of platinum, the lower positive electrode may be made of a carbon or a thin iron rod.

This form of the arc has been officially adopted by spectroscopists for work on secondary and tertiary standards, particularly in the case of the iron lines. At the meeting of the International Union for Co-operation in Solar Research held at Bonn in 1913, it was agreed that the following be the standard conditions for using the Pfund iron arc in air :—[1]

1. The length of the arc to be 6 mm.
2. For wave-lengths greater than 4000 A. the current to be 6 amperes, and for wave-lengths less than 4000 A. the current to be 4 amperes, or less if possible.
3. A direct current to be used at 220 volts, the upper electrode being made positive.
4. The rays to be used from the central portion of the arc 2 mm. in width.
5. Only those iron lines to be measured which belong to classes *a*, *b*, *c*, *d* of the Mount Wilson classification.

At the meeting of the International Astronomical Union at Rome in 1922, this body having taken over the programme of the older body, the following were adopted as standard conditions for the use of the Pfund iron arc :—[2]

In order to obtain lines of constant wave-length, constant intensity distribution, and adapted to high orders of interference, the Pfund arc shall be operated with 5 amperes or less at 110 to 250 volts and a length of 12 to 15 mm. A central zone to be used at right angles to the axis of the arc, not to exceed 1 to 1·5 mm. in width. The arc to be operated with an iron rod 6 to 7 mm. in diameter as the upper pole, and a bead of iron oxide as the lower pole.

These modifications were introduced to guard against the pole effect or wave-length difference which appears in the case of many lines according to whether the arc is examined near the poles or at the centre. This pole effect, and also the Mount Wilson classification of the iron lines, will be discussed in the following section.

[1] *International Union for Co-operation in Solar Research*, *Trans.*, **4**, 59 (1914).
[2] *International Astronomical Union*, *Trans.*, **1**, 36 (1922).

Mention may be made of two other devices for obtaining arc spectra in air. In one of these, Crew and Tatnall [1] use as one electrode a rapidly revolving disc mounted on the armature of a small electric motor. This disc carries, fixed round its periphery, small pieces of the metal under investigation. The other electrode is a rod of the same metal mounted on a fine-cut screw, in order that its position may be accurately adjusted. To obtain the arc discharge the motor is started and the current turned on, and then the second electrode is slowly pushed forward until it just touches the projecting pieces on the rotating disc. By this means the arc is spread out fanwise in a manner that is very convenient for spectroscopic examination. An alternating current of 2 to 10 amperes is used at 100 volts.

As was stated on p. 32, Fabry and Perot,[2] in their work on the absolute wave-lengths of certain metallic spectrum lines by their interferometer methods, employed an apparatus which they called a "trembleur." This consisted of two pole pieces of the metal under investigation, one of which was fixed, whilst the other was mounted on a spring which was maintained in a state of oscillation by means of an electro-magnet. The design was very similar to that of the hammer break on an induction coil. Every time the metal poles came into contact the arc was struck between them. The whole apparatus was mounted in a vacuum.

So far, we have only considered the methods of obtaining the arc spectra of metals, and when other substances, such as metallic salts, are to be investigated it is usual to use the carbon arc and to feed the salt into it. This may be done by making the lower pole positive and by introducing the salt, in small quantities at a time, into the crater which is formed in this pole. This generally upsets the stability of the arc, causing it to flicker badly and to jump from side to side. This is very vexatious, since the whole success of the operation depends on the maintenance of an image of the arc on the slit of the spectrograph.

A more satisfactory method is to use as the lower positive pole a cored carbon, that is to say, a carbon rod with a central hole bored along its length. This hole is packed with the substance in question, the negative pole being an ordinary solid rod. Hemsalech and de Watteville [3] suggested two methods for introducing the substance into the central hole of the positive carbon. In the first, a mixture of three parts of boron trioxide and one part of the substance is melted and poured into the hollow bore, and in the second, two parts of the substance and one part of asbestos and sodium silicate cement is pressed into the bore.

Liveing and Dewar, in their pioneer investigations in emission spectra, enclosed the arc in a block of lime or similar refractory substance.[4] They used a cubical block, bored horizontally with four holes at right angles to one another and one vertical hole to the

[1] *Phil. Mag.*, **38**, 379 (1894).
[2] *Comptes Rendus*, **130**, 406 (1900).
[3] *Ibid.*, **145**, 1266 (1907).
[4] *Proc. Roy. Soc.*, **28**, 352 (1879).

junction of the four horizontal borings. The carbon poles for the arc passed through an opposite pair of the horizontal borings and the substance to be investigated was fed with the arc down the vertical boring. The radiation from the arc passed through a third horizontal boring to the spectroscope, whilst any desired gas could be introduced through the fourth horizontal boring.

For many purposes great advantage is gained by maintaining the arc in a vacuum, and this method has been adopted by many investigators. For example, Fowler and Payn [1] studied the spectra of magnesium, zinc, cadmium, and iron, as given by the arc burning in an exhausted vessel. Loving [2] also adopted the same method for the study of the spectra of magnesium, calcium, chromium, manganese, and iron. More recently a vacuum arc has been described by Nagaoka and Sugiura [3] based on the use of a modified Wehnelt cathode, which originally consisted of a strip of platinum coated with some metallic oxide, such as that of calcium or barium. This arc is singularly well adapted for the emission of spectrum lines of great purity, such as are required for accurate wavelength determination by interference methods.

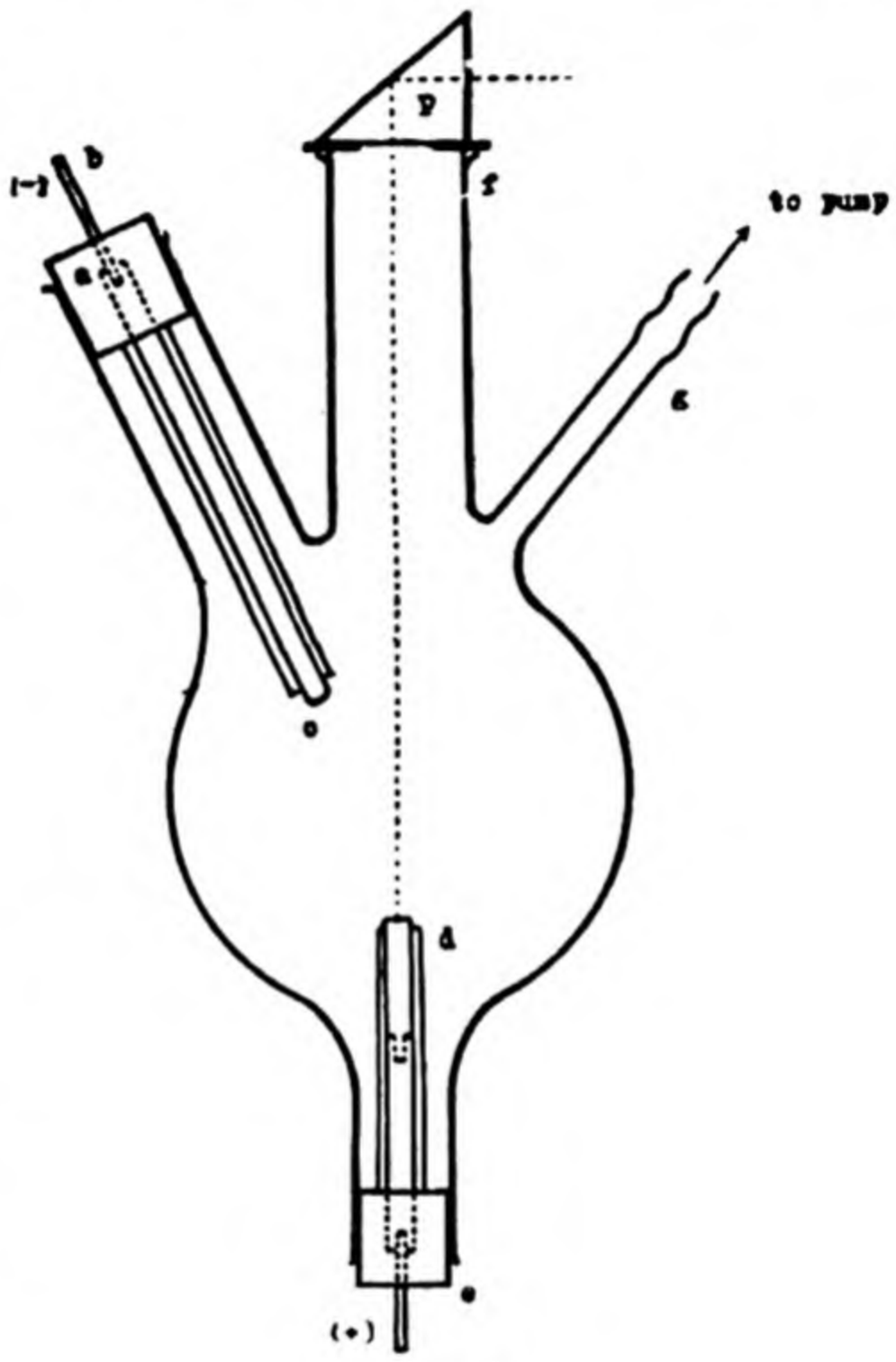


FIG. 34.

The apparatus is shown in Fig. 34, and consists of a three-necked flask of about 1 litre capacity. The cathode is a carbon rod C, which is enclosed in a tightly fitting silica tube, the end of the rod only being exposed. This carbon rod is mounted in an india-rubber stopper *a*, and a thick copper wire *b* is screwed into the rod to make contact. The stopper is covered with Khotinsky cement in order to make it air-tight. The carbon rod, after a preliminary heating, is dipped in a solution of strontium and barium nitrates and then again heated in a Bunsen burner, so that it becomes coated with a white layer of the oxides.

The substance to be tested is placed in the upper end of the silica tube *d*, which also contains a carbon rod, as shown. This carbon rod has a stout copper wire screwed into it, and is mounted in the india-rubber stopper *e*, which is coated with Khotinsky cement. The upper end of the neck *f* is ground flat, and a right-angle prism of quartz is cemented on to it, the apparatus being exhausted through the side

[1] *Proc. Roy. Soc.*, **72**, 253 (1903). [2] *Astrophys. Journ.*, **22**, 285 (1905).
[3] *Ibid.*, **57**, 86 (1923).

tube *g*. The exhaustion is carried as far as possible by means of a mercury vapour diffusion pump and a mechanical fore-pump.

The arc is started in the following way : The carbon rod cathode and the anode are connected to the cathode and anode of a small induction coil, when the carbon cathode becomes surrounded with a glow discharge. The two electrodes are then rapidly connected with the poles of a 500-volt direct current generator and the current adjusted to the proper strength, which varies with the substance under examination. With most metals, 2 to 3 amperes and a terminal voltage of 90 to 80 volts are sufficient to give an intensely bright discharge, the current remaining very constant. In order to obtain very intense illumination the terminal voltage may be increased to 150 volts and the current to 5·5 amperes, but the evaporation of the anode material becomes very rapid.

In order to guard against too great a rise in temperature and the softening of the cement, the flask is immersed to about two-thirds in a trough of running water. There is at times considerable deposition on the glass walls of the flask, and care must be taken to protect the lower face of the right-angle prism. This can be done by the use of diaphragms in the neck of the flask below the prism.

There is no difficulty in obtaining with this apparatus the spectra of highly refractory metals, such, for instance, as tungsten. So long as the current is not broken, the light continues to be emitted until the greater part of the anode material is evaporated. When this stage has been reached, it is difficult to re-light the lamp. Both salts and oxides of metals can be used as anode material.

The purity of the spectrum was tested by comparison of the spectrum of electrolytic iron given by the vacuum arc with that of the Pfund arc, the radiations being analysed by means of a Fabry and Perot étalon and a quartz spectrograph. The fringes obtained with the rays from the vacuum arc are much more sharp and more easy to measure than those given by the rays from the Pfund arc. There is no question but that this vacuum arc is admirably adapted as a source of rays when accurate wave-length determinations are to be made or the structure of the individual lines is to be investigated.

There is one interesting characteristic of the vacuum arc which must be mentioned. With lower values of current the cyanogen band spectrum is very strongly developed and interferes considerably with the investigation of metallic lines in the region of these bands. As the current strength is increased the intensity of these bands decreases, and when a certain current strength is exceeded they vanish and the metallic spectrum lines only are visible.

The arrangement of the cathode and anode in this apparatus is exactly analogous to that of a Coolidge X-ray tube, and, indeed, if the potential difference between the two electrodes in the vacuum arc be sufficiently high, X-rays must be emitted. By the use of the current from a small step-up transformer, rectified by means of a kenotron, a potential difference of 1500 volts was maintained between

the electrodes. Three strips of thin aluminium foil were placed one above the other, so that they formed layers of three different thicknesses, and laid on the film of a photographic plate. The whole was then wrapped in black paper and placed in the neck of the flask under the right-angle prism and exposed to the rays for 15 minutes. Zinc, silver, and mercury were used as anodes. On developing, the plate was blackened each time, gradations of intensity being obtained corresponding to the thickness of the aluminium foil. Using the wing of a butterfly, it was found that the veins screened the photographic action. It was calculated that the wave-length of the X-rays is a little less than 10 A. With a terminal voltage of 80 volts, no effect was produced on the photographic plate in spite of the fact that the light emitted by the discharge was very intense.

The vacuum arc, such as has been described, involving the arc discharge between metallic poles in a vacuum, has been developed in a very remarkable way, resulting in the production of the mercury vapour lamp. In essence this lamp is a true vacuum arc, since the illumination is obtained by the passage of an arc discharge between two surfaces of mercury, but the lamp stands perhaps in a class by itself on account of the great number of uses to which it is applied. Although this type of apparatus, strictly speaking, is a vacuum arc, it will be preferable to speak of it as a lamp, which is the term generally used at the present time. The basic characteristic of this type of apparatus is that a metal is employed which is volatile enough to give a vapour of sufficient density to conduct the current. Besides the mercury vapour lamp, a cadmium lamp was used by Hamy, and also by Michelson in his classic work on the wave-lengths of the cadmium lines.

The Hamy [1] lamp consists of a glass tube 20 mm. in diameter, 130 mm. long, sealed at both ends, with a central capillary portion. A few centigrammes of cadmium are introduced through a side tube, which is then attached to a good exhaust pump. The whole tube is heated to about 300° and thoroughly exhausted, and then the tube is sealed off. External electrodes are used, each end of the tube being covered with a brass cap packed with powdered graphite. The whole tube is heated as follows: it is suspended in a somewhat larger copper tube, which rests in a copper trough heated by a row of Bunsen burners. It is not truly accurate to speak of this apparatus as a vacuum arc because a high potential discharge is necessary owing to the resistance set up by the glass walls.

One of the earliest forms of mercury vapour lamps was devised by Arons,[2] and is shown in Fig. 35. It consists of an inverted U tube B, with a platinum wire sealed in at each end at *m* and *n*. Two bulbs were blown on outside the ends of the tube B, and these are filled with mercury, connection with the electric power being made by wires

[1] *Comptes Rendus*, **124**, 749 (1907).
[2] *Ann. der Phys.*, **47**, 767 (1892); **58**, 73 (1896).

through the small side tubes, as shown. The tube B is exhausted as completely as possible, all gases being removed from the mercury by the application of heat. The discharge is started by tilting the lamp until the two mercury surfaces are brought momentarily into contact. This particular design of the mercury lamp is now only of historic interest. Mention may, however, be made of Arons' statement that if certain metals, such, for instance, as zinc or cadmium, are dissolved in the mercury, the discharge radiates the lines of these metals as well as those of mercury.

We may next consider two forms of the mercury lamp which may easily be constructed in the laboratory.

Barnes [1] has devised a very convenient form of lamp, which is shown in Fig. 36. Through the neck D of the globular vessel A, which is about 800 c.c. in volume, passes the iron tube E, of diameter 13 mm. Along the centre of this passes the porcelain tube F, 8 mm. in diameter. This porcelain tube is connected with a glass tube, which in turn is connected with a large rubber tube. Mercury fills the space between the porcelain and iron tubes, as well as the porcelain, glass, and rubber tubes attached. The electric wires are attached one to the iron tube E and the other to the mercury in the porcelain tube F. The opening B is closed by a glass or quartz plate, and the whole bulb is exhausted through C. By raising the mercury column until a drop flows over into E the arc is started, and any further adjustments are easily carried out by raising or lowering the mercury column. Barnes employed with this apparatus a current of 4 amperes at 110 volts, and found that, although mercury was deposited all over the walls of the apparatus, none reached the window at B.

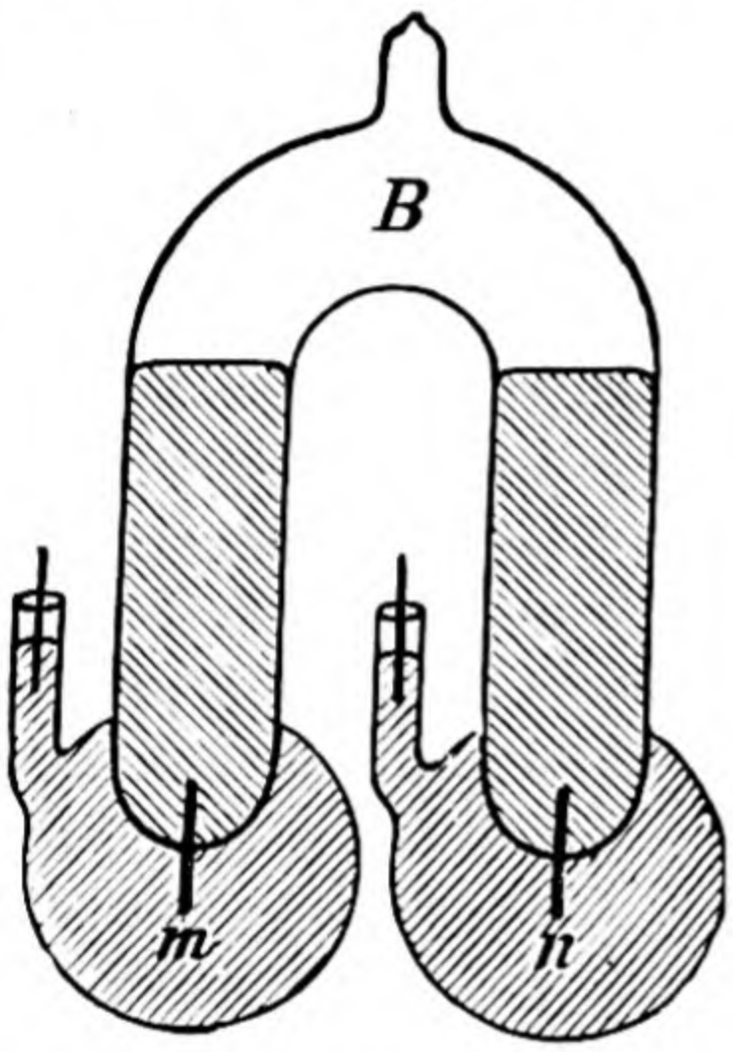


FIG. 35.

A very simple form of mercury lamp has been described by Pfund,[2] which can easily be made by any one familiar with the elements of glass blowing. The lamp is shown in Fig. 37, and consists of a piece of glass tubing, 7 cm. long and 1·2 cm. in diameter, to which there is sealed a larger tube 18 cm. long and 3 cm. in diameter. The upper end of this larger tube is ground flat, and a quartz plate is attached by means of sealing wax. A side tube is sealed on to the larger tube for the purposes of exhaustion. A platinum wire is sealed into the lower end of the smaller tube, which is then filled with mercury to a height of about 3 cm. The mercury forms the negative electrode, while a hollow sheet-iron electrode forms the positive. This electrode

[1] *Astrophys. Journ.*, **19**, 190 (1904).

[2] *Ibid.*, **27**, 299 (1908).

is made by cutting out a piece of sheet iron to the shape shown in Fig. 38*a*, and this is subsequently bent into the form shown in Fig. 38*b*. It is important that the lower portion of this electrode be of smaller

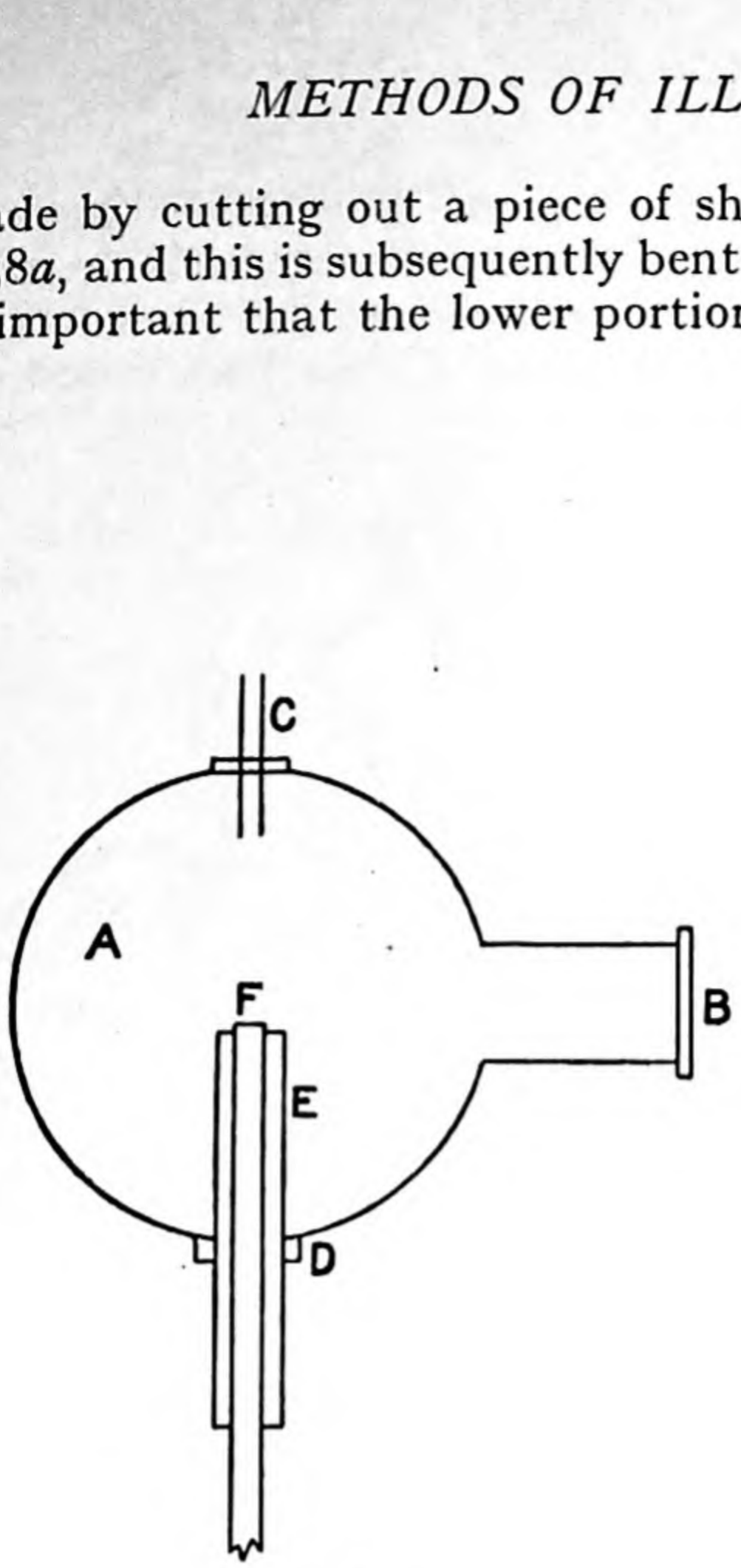


FIG. 36.

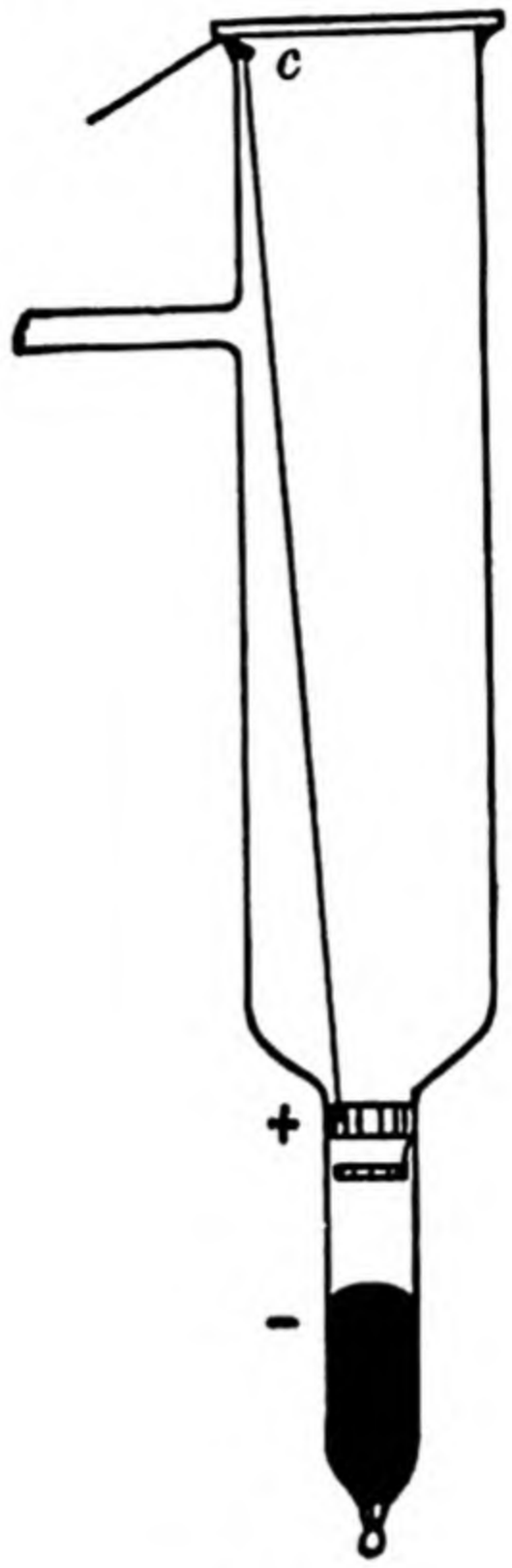


FIG. 37.

diameter than the upper, so that it does not touch the glass tube at any point. This electrode is held in place by friction against the glass tube about 1 cm. above the mercury. An iron wire is attached to the electrode, and at the point *c* (Fig. 37) a piece of copper wire is fused to the iron, and the copper wire passes out of the tube through the sealing-wax junction. It is necessary that the copper wire be covered with shellac to guard against its being amalgamated by the mercury vapour. The lamp is used in a vertical position, and takes from 1·4 to 1·6 amperes at 110 volts direct current. The lower, mercury-filled portion is heated by means of a Bunsen burner, and the arc is started either by tilting the lamp or by jerking it so that momentary contact is made between the two electrodes. It is best to run the lamp for some time while it is still on the pump after the exhaustion has been carried as high as possible. In this way most of the water vapour and gases contained in the electrodes can be removed. Then, after

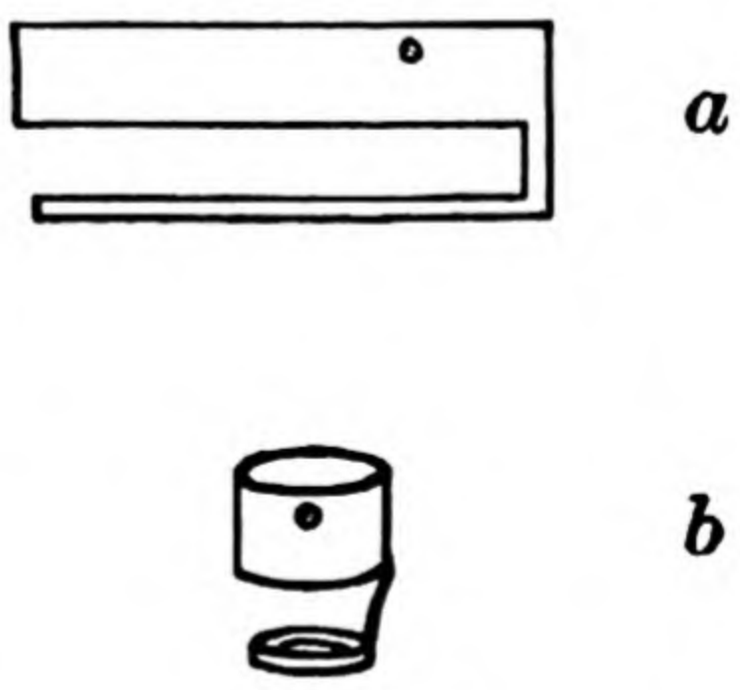


FIG. 38.

carrying the exhaustion to as high a point as possible, the lamp is sealed off. It will generally be found after the lamp has been in use for some time that more gases are liberated, and the arc becomes so hot as to melt the glass. It is well to test this from time to time

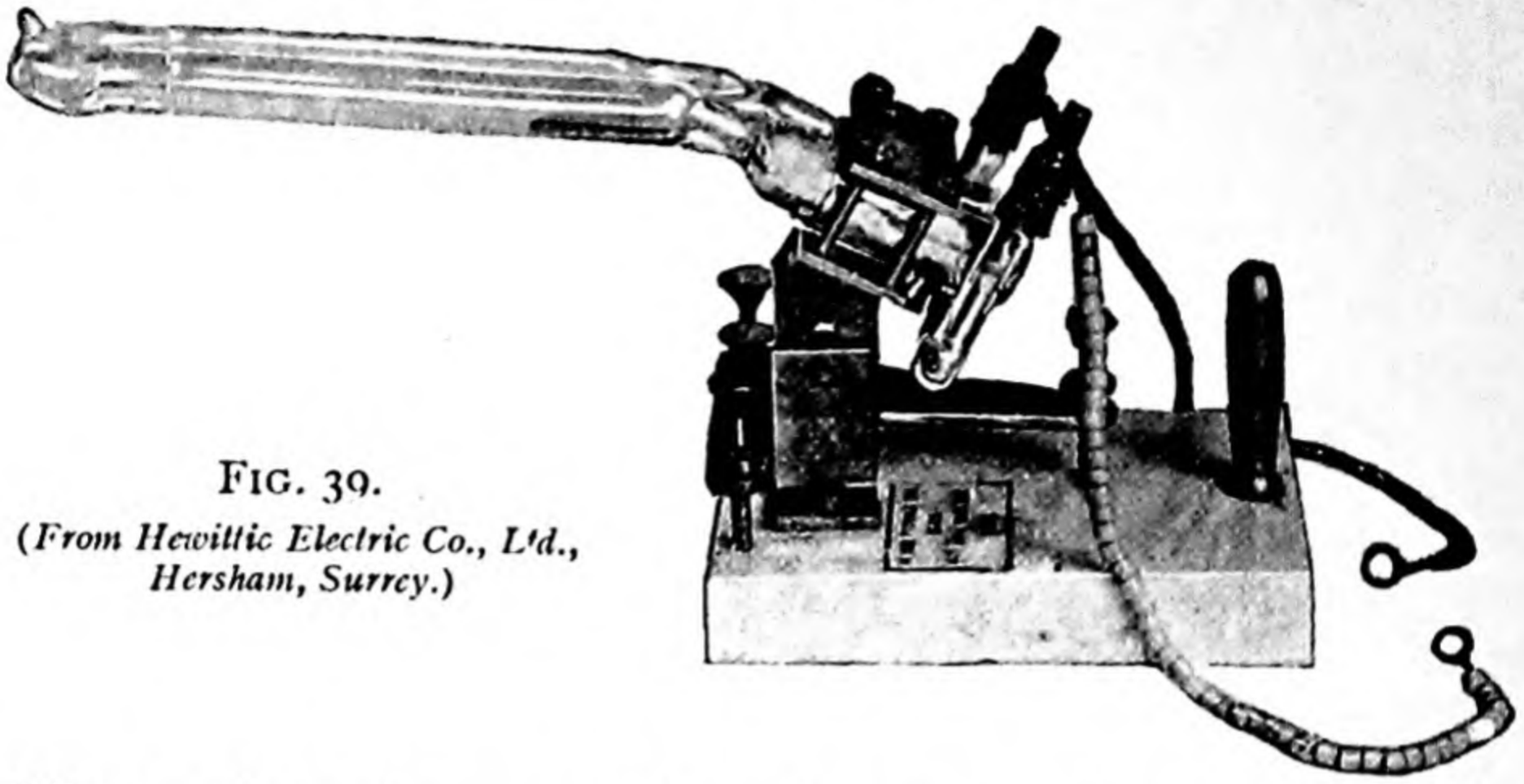


FIG. 39.
(From Hewittic Electric Co., Ltd., Hersham, Surrey.)

by holding a piece of paper against the glass. If the paper is charred the lamp should be re-exhausted.

Mercury vapour lamps made of glass and of quartz are now manufactured by several commercial firms, and are used for numerous purposes. The general construction of these lamps is similar to that

FIG. 40.
(From Hewittic Electric Co., Ltd., Hersham, Surrey.)

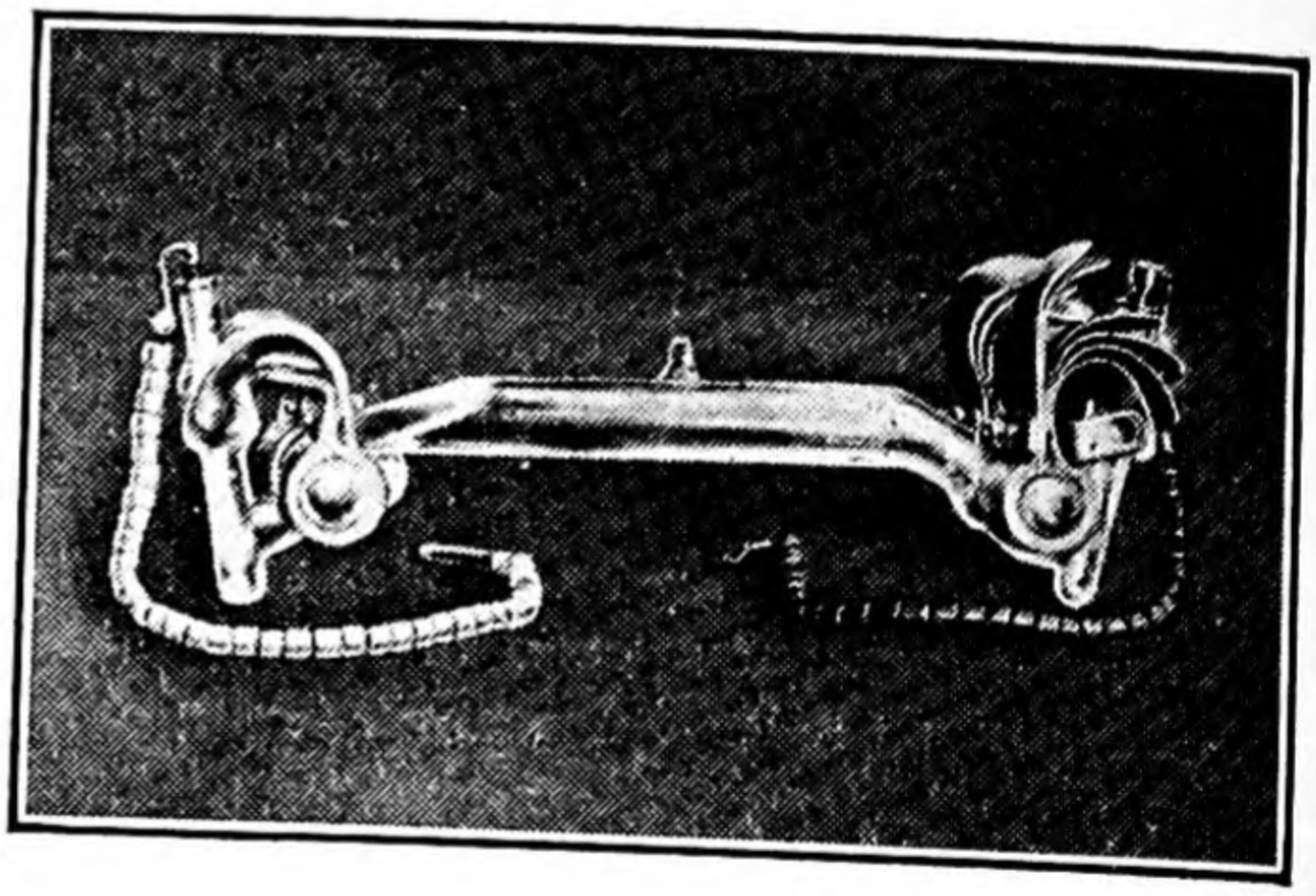


FIG. 41.
(British Hanovia Quartz Lamp Co., Ltd., Slough.)

of the Arons lamp in that the arc is struck by tilting the lamp until the two mercury surfaces come into contact, which is broken on restoring the lamp to its normal position. In Figs. 39, 40, and 41 [1] are shown three of the most usual designs.

[1] For permission to reproduce these I am indebted to the Hewittic Electric Company, Hersham, Surrey, and to the British Hanovia Quartz Lamp Company, Ltd., Slough, England.

The quartz mercury lamps are, as a rule, made of three types, for use with 110, 220, and 500 volts direct current, respectively. It is not possible here to indicate the manifold uses of these lamps, but mention may be made of the value of the mercury lines for observations with the refractometer, polarimeter, and other branches of physics, which are not very far removed from spectroscopy. They also are used in photochemical work, which, of course, is based on absorption spectra. Then again, they are giving most valuable results in what, after all, is a type of photochemistry, namely, light therapy and the treatment of disease.

For some years past quartz mercury lamps have been used in my laboratories, and an account of the results of our experience may not be out of place. It is, perhaps, not unnecessary to speak a word of warning against working with these lamps without wearing dark spectacles. I have heard it stated that there is little danger during the first minute after the lamp has been lighted. This may be true for some people, for there is considerable variation in sensitiveness of the eyes of different persons, but I have come across one case of acute arc blindness caused entirely by the radiation of newly-lighted lamps. A false sense of security may be felt by the inexperienced, since the inflammation in the majority of cases does not commence until from 1 to 2 a.m. in the following morning.

There is one feature of these lamps which brings into prominence a remarkable property of fused quartz glass. When a new lamp is started, a strong smell of ozone is developed, owing to the photochemical action of the very short wave-length radiations $\lambda = 2001{\cdot}6$ to $\lambda = 1872{\cdot}2$, emitted by the lamp, on the surrounding oxygen of the atmosphere. In the case of the low-power lamps burning at 110 volts, this formation of ozone slowly decreases until after some days' use of the lamp it ceases altogether. This is due to the fact that the quartz walls of the lamp no longer are able to transmit rays of very short wave-length. The phenomenon is familiar to any one who has had experience with these lamps.

In a lengthy investigation of a series of photochemical reactions which are stimulated by radiations varying from $\lambda = 3000$ to $\lambda = 1900$ we have experienced this development of opacity by quartz to ultra-violet light, and at first found considerable difficulty in explaining results, which appeared to be extraordinarily elusive. In one experiment large volumes of solution were exposed to the radiation from quartz mercury lamps set inside quartz sleeves, which were immersed in the solution. The progress of the photochemical reaction was determined by tests made each day, and at first the yield of the products was proportional to the time of exposure. After about ten days the velocity of the reaction began to decrease, until it fell to zero on about the fourteenth day. There was no apparent reason for this until, on dismantling the apparatus, it was found that the quartz sleeves had developed an amethystine colour. The appearance of this colour indicated that the quartz had been partly converted into

a condition with a power of absorbing ultra-violet light, since the colour was visible by transmitted light. In other words, the quartz had become opaque to ultra-violet light. In view of the probability that this condition was metastable, the effect of heating the quartz was tried, and when the sleeves were heated in a powerful blast flame they emitted a brilliant green phosphorescence, which gradually faded away. It was then found that the amethyst colour had disappeared and that the quartz had apparently regained its original transparency to ultra-violet radiation.

There is no doubt that in this phenomenon is to be found the explanation of the deterioration of the quartz mercury lamps as sources of ultra-violet radiation, and also of the fact that the 220-volt lamp does not deteriorate in the same way as the 110-volt lamp, the reason of this superiority of the former being due to the much higher temperature reached by the quartz walls during the operation of this lamp.

Some further work on a photochemical reaction, which is known to require for its stimulation the shortest wave-length radiation emitted by these quartz lamps, has proved that the opacity to the ultra-violet developed by the quartz glass on exposure to ultra-violet radiation commences at $\lambda = 1876$, and slowly extends up the spectrum towards the longer wave-lengths. A quartz glass vessel becomes completely opaque to the very short waves after four hours' exposure to the radiation of a 220-volt quartz mercury lamp at a distance of 3 inches. The transparency can be restored by the heat treatment, the same phosphorescent emission being observed. An unexpected accident emphasised the metastable nature of the condition when the quartz is opaque to ultra-violet light. Some quartz test tubes which had been exposed to the light for some hours were accidentally dropped on to the stone floor of a dark laboratory. The brilliance of the phosphorescence was very striking.

This phenomenon does not seem to consist of a single process. Professor F. C. Drummond tells me that he has observed a marked action on a photographic plate given by quartz after exposure for half an hour to ultra-violet light. This observation, which we have been able to confirm, indicates that an unstable condition is first established which reverts with the evolution of actinic radiation to the normal. After several hours' exposure the unstable condition becomes more permanent, and it is doubtful whether complete restoration to the normal state takes place without heating. The amethystine-coloured state seems to be completely metastable, since quartz tubes brought into this state remain unchanged after one year's interval.

Then again, we have found that in some cases an intermediate state of metastability can be established. A number of quartz tubes were used for a photochemical reaction for some months, the heat treatment being applied at frequent intervals. Towards the end of this period the tubes lost the power of recovery on being heated and

remained permanently opaque to the extreme ultra-violet rays. After remaining in the dark for one year, however, many of these tubes seemed entirely to regain their transparency.

These changes have an important bearing on the efficiency of the quartz mercury lamp as a source of very short ultra-violet radiation. The rapid deterioration of the 110-volt lamp has already been mentioned. In the case of the 220-volt lamp the radiating power in the extreme ultra-violet remains sensibly constant for some time, a fact which can be recognised from the ready formation of ozone in the immediate neighbourhood of the lamp. After continued use for five to six months (the actual period is indefinite), the lamp markedly deteriorates in its power of radiating the extreme ultra-violet rays, in spite of the relatively high temperature of the quartz walls. The lamp seems, however, to regain its original power after being kept for a year without being used. It must be remembered that so far as the 220-volt lamp is concerned, the deterioration is confined to the extreme ultra-violet region. Its value for therapeutic work is probably not impaired, but it may be found that the relation between dosage and the symptoms of erythema may be altered, since the latter is doubtless caused by the extreme ultra-violet rays.

I feel that these results are of some interest from the theoretical standpoint, but the consideration of this must be postponed until Chapter IV.

The Mount Wilson Classification of the Iron Lines.—In dealing with the Pfund arc, the conditions were given which have been officially adopted by spectroscopists for the use of this arc in the determination of secondary and tertiary standard wave-lengths in the spectrum of iron. In describing the general and special methods of arc spectra we have not in any way discussed the difference in the characteristic properties of the lines which are found in the arc spectrum of an individual element. These variations in the nature of the lines become of great importance in the case of the iron spectrum, which has been adopted as the basis of the international system of standard wave-lengths. In addition to the specific limitations which have been set to the conditions of using the Pfund arc as to orientation, locus of radiation, and current, there is the restriction which has been set to the number of lines in the iron spectrum which justify an international confidence in their constancy of wave-length.

It must be understood that these restrictions and limitations are not by any means arbitrary, but that they have their origin in thoroughly sound scientific work, and I feel that a brief account of this work should find a place here. Reference has more than once been made to the fact that a certain number of the lines in the spectrum of iron are not suitable for use as wave-length standards, this being due to the fact that these particular lines are extraordinarily sensitive. Their wave-length changes appreciably with small changes of pressure, and one cannot but realise that the exclusion of these lines from serving as members of a union of standards is a striking index

of the very remarkable advances made by spectroscopy in recent years.

The origin of the present situation as regards the iron spectrum lines is the discovery by Humphreys [1] that in general the wave-lengths of lines are altered when the pressure of the atmosphere in which the excitation takes place is increased. Humphrey's work, together with that of other investigators, will be described in Vol. IV., and it is sufficient to say here that the pressure-shift is by no means a constant, and varies not only with the wave-length, but also with the particular series to which a line belongs. In the case of iron, where until quite recently nothing was known of any series relationships, the phenomenon naturally took on an aspect of complexity. As far as the problem of wave-length standards is concerned, it is not the question of series relationships which interests us, for the important question arises as to whether under the normal conditions of excitation there occur pressure gradients sufficiently steep to cause measurable changes in the wave-lengths of any of the lines of the spectrum which we have adopted as the standard. In other words, are any of the iron lines so sensitive to pressure changes that they cannot be used as standards? The question was answered in the affirmative by Gale and Adams,[2] who studied the effect of moderate pressures on the wave-lengths of many of the iron and titanium lines.

As the result of the work on the pressure effect in general it is known that lines may be divided into five main classes :—

1. Lines which are symmetrically reversed.
2. Lines which are unsymmetrically reversed.
3. Lines which remain bright and fairly narrow under pressure.
4. Lines which remain bright and symmetrical, but become wide and diffuse under pressure.
5. Lines which remain bright and are widened very unsymmetrically towards the red.

The method of investigation adopted by Gale and Adams was to make as complete a study as possible of all well-measurable lines at a single pressure, and for the other pressures to use a selected list of lines sufficient in number to give a mean of high precision for purposes of comparison. The pressure adopted for the principal series was 8 atmospheres above atmospheric pressure, the other pressures being 2, 4, 6, 12, and 16 atmospheres above atmospheric pressure.

In Table X. are given the wave-lengths and pressure displacements measured at 8 atmospheres of the lines observed by Gale and Adams. The second column contains the class of the line according to the above system of classification, the third column contains the group to which each line is assigned, this being explained below, whilst the fourth column shows the change in wave-length observed.

[1] *Astrophys. Journ.*, 4, 249 (1896). [2] *Ibid.*, 35, 10 (1912).

TABLE X.

λ.	Class.	Group.	Δλ.	λ.	Class.	Group.	Δλ.
6678·235	4	b	0·086	5393·375	5	d	0·14
6594·121	4	b	0·070	5371·734	1	a	0·029
6593·161	4	b	0·076	5341·213	4	a	0·028
6546·479	4	b	0·073	5340·121	5	d	0·14
6495·213	4	b	0·065	5333·089	4	a	0·029
6431·066	4	b	0·068	5328·696	4	a	0·026
6421·570	4	b	0·068	5328·236	1	a	0·029
6411·865	5	d	0·23	5324·373	5	d	0·12
6400·217	5	d	0·24	5270·558	4	a	0·029
6393·820	4	b	0·072	5269·723	1	a	0·027
6337·048	5	d	0·26	5266·738	5	d	0·13
6335·554	4	b	0·074	5233·122	5	d	0·11
6318·239	4	b	0·080	5227·362	4	a	0·031
6301·718	5	d	0·25	4957·785	5	c	0·086
6298·007	4	b	0·068	4957·480	5	c	0·083
6265·348	4	b	0·070	4920·685	5	c	0·082
6256·572	4	b	0·089	4919·174	5	c	0·072
6254·456	4	b	0·064	4891·683	5	c	0·052
6252·773	4	b	0·077	4890·948	5	c	0·070
6246·535	5	d	0·28	4878·407	5	c	0·087
6230·943	4	b	0·070	4872·332	5	c	0·094
6219·494	4	b	0·073	4871·512	5	c	0·080
6213·444	4	b	0·072	4859·928	5	c	0·100
6200·527	4	b	0·079	4531·327	3	b	0·029
6191·779	4	b	0·086	4528·798	4	c	0·061
6173·553	4	b	0·067	4494·738	4	c	0·053
6157·945	4	b	0·041	4489·911	3	a	0·015
6137·915	4	b	0·078	4476·185	4	b	0·021
6136·829	4	b	0·082	4466·727	4	b	0·018
6065·709	4	b	0·077	4461·818	3	a	0·015
6027·274	4	b	0·062	4459·301	4	c	0·051
5975·575	4	b	0·054	4454·552	3	b	0·023
5659·052	5	d	0·15	4447·892	4	c	0·051
5638·488	5	d	0·15	4443·365	3	b	0·019
5624·769	5	d	0·16	4442·510	4	c	0·053
5615·877	5	d	0·13	4430·785	4	c	0·048
5603·186	5	d	0·15	4427·482	3	a	0·017
5586·991	5	d	0·12	4422·741	3	b	0·018
5576·320	5	d	0·16	4415·293	1	b	0·018
5573·075	5	d	0·14	4408·582	4	c	0·058
5569·848	5	d	0·14	4407·871	4	c	0·053
5535·644	4	a	0·034	4404·927	1	b	0·021
5507·000	3	a	0·031	4383·720	1	b	0·027
5501·683	3	a	0·030	4376·107	3	a	0·018
5497·735	3	a	0·030	4369·941	3	b	0·023
5476·778	5	d	0·11	4352·908	3	b	0·017
5476·500	4	a	0·029	4337·216	3	b	0·027
5455·834	4	a	0·029	4325·939	1	b	0·020
5447·130	4	a	0·031	4315·262	3	b	0·019
5434·740	4	a	0·027	4308·081	1	b	0·021
5429·911	4	a	0·029	4299·410	5	d	0·09
5405·989	4	a	0·027	4294·301	2	b	0·029
5397·344	4	a	0·029	4291·630	3	a	0·014

TABLE X.—*Continued.*

λ.	Class.	Group.	Δλ.	λ.	Class.	Group.	Δλ.
4282·565	1	b	0·021	3887·196	1	b	0·022
4271·934	1	b	0·022	3886·434	1	a	0·011
4260·640	2	c	0·051	3834·364	1	b	0·016
4250·945	2	b	0·022	3827·980	1	b	0·019
4250·287	5	c	0·070	3826·027	1	b	0·021
4236·112	5	d	0·09	3815·987	1	b	0·024
4233·772	5	d	0·09	3795·147	1	b	0·015
4227·606	5	d	0·11	3788·046	1	b	0·016
4216·351	3	b	0·015	3767·341	1	b	0·017
4210·494	5	c	0·053	3765·689	1	b	0·013
4204·101	3	b	0·017	3763·945	1	b	0·017
4202·198	1	b	0·025	3758·375	1	b	0·022
4144·038	1	b	0·029	3749·631	1	b	0·017
4134·840	4	b	0·027	3748·408	1	a	0·010
4132·235	1	b	0·024	3746·058	1	a	0·008
4071·908	1	b	0·021	3745·717	1	a	0·008
4063·759	1	b	0·020	3743·508	1	b	0·015
4045·975	1	b	0·023	3737·281	1	a	0·016
4005·408	1	b	0·019	3735·014	1	b	0·013
3997·545	4	b	0·015	3733·469	1	a	0·007
3977·891	4	b	0·017	3727·778	1	b	0·014
3969·413	1	b	0·022	3722·729	1	a	0·010
3956·819	4	b	0·014	3720·084	1	a	0·014
3930·450	1	a	0·013	3709·389	1	b	0·013
3928·075	1	a	0·012	3705·708	1	a	0·007
3923·054	1	a	0·011	3687·610	1	b	0·016
3920·410	1	a	0·010	3680·069	1	a	0·007
3906·628	1	a	0·011	3647·988	1	b	0·012
3903·090	1	b	0·022	3631·605	1	b	0·015
3899·850	1	a	0·012	3618·919	1	b	0·011
3895·803	1	a	0·011	3609·008	1	b	0·008
3888·671	1	b	0·020				

Now we have already dealt with the low temperature lines of iron, these usually being known as the flame spectrum lines. The most prominent of these lines which were observed by Gale and Adams are given in Table XI., together with their pressure displacements.

TABLE XI.

λ.	Δλ.	λ.	Δλ.	λ.	Δλ.	λ.	Δλ.
5507·000	0·031	5371·734	0·029	4291·630	0·014	3746·058	0·008
5501·685	0·030	5341·213	0·028	3930·450	0·013	3745·717	0·008
5497·735	0·030	5333·089	0·029	3928·075	0·012	3737·281	0·015
5476·778	0·029	5258·236	0·029	3923·054	0·011	3733·469	0·007
5455·834	0·029	5269·723	0·027	3920·410	0·010	3722·600	0·010
5447·130	0·031	5227·362	0·031	3906·628	0·011	3720·084	0·014
5434·740	0·027	4489·911	0·015	3899·850	0·012	3705·708	0·007
5429·911	0·029	4461·818	0·015	3895·803	0·011	3680·069	0·007
5405·989	0·027	4427·482	0·017	3886·434	0·011		
5397·344	0·029	4376·107	0·018	3748·408	0.010		

A comparison with the observations recorded in Table X. shows at once that the displacements of these flame lines are markedly smaller than those of the other lines observed in the same region. The measurement of King [1] on the effect of pressure on the electric furnace spectrum of iron show that the same difference between the flame lines and the other lines exists also in this source.

Gale and Adams plotted all the displacements which they observed at 8 atmospheres against wave-lengths, and it was seen that certain groups of lines, for which the average displacements differ widely, apparently belong together. Furthermore, it was clear that the flame lines must be considered as a separate group. They found in this way four groups of lines indicated in Table X. by *a*, *b*, *c*, *d*.

Group *a* includes all the flame lines and two or three additional lines in the yellow region, which may be flame lines, but for which observations are lacking.

Group *b* is a large group and includes all the lines showing small displacements which are not included in group *a*.

Group *c* consists of lines showing much larger displacements than those shown by the lines in group *b*. These lines are all bright under pressure and, especially in the green region, unsymmetrical and difficult to measure.

Group *d* consists of a few lines in the violet, a fair-sized group in the greenish-yellow, and a small number in the red, all of which show very large displacements. The average displacements for the four groups have the following ratios : 1 : 1·5 : 3·4 : 6·6, and, further, the displacements within each group vary with the cube of the wave-length.

This work by Gale and Adams is of very great importance because, although relatively few of the iron spectrum lines were investigated and described in this paper, it established different grades of sensitiveness of these lines. The next step was taken by St. John and Ware,[2] who examined the international secondary standards of wave-length in the spectrum of iron from $\lambda = 5506$ to $\lambda = 4282$ as to their consistency amongst themselves, and also determined the wave-lengths of 198 lines as tertiary standards between $\lambda = 5506$ and $\lambda = 4118$.

These authors came to the conclusion that their results were closely related to the classification of the iron lines set up by Gale and Adams, and they extended the classes and groups. The classes adopted by St. John and Ware are :—

1. Lines which are symmetrically reversed.
2. Lines which are unsymmetrically reversed.
3. Lines which remain bright and fairly narrow under pressure.
4. Lines which remain bright and symmetrical but become wide and diffuse under pressure.
5. Lines which remain bright and are widened very unsymmetrically towards the red.
6. Lines which remain bright and are widened very unsymmetrically towards the violet.

[1] *Astrophys. Journ.*, **34**, 37 (1911).

[2] *Ibid.*, **39**, 5 (1914).

The groups adopted are :—

Group *a*.—This includes the flame lines ; all the lines of this group show small pressure displacements.

Group *b*.—This is a large group, including all lines of moderate displacement, and is probably complex.

Group *c*.—This consists of lines showing much larger displacements than those of group *b*, and includes two fairly large classes.

Group *d*.—This is made up of lines showing immense displacements and unsymmetrical widening towards the red under pressure. St. John and Ware divided this group into *d* and sub-*d*, the lines of the latter showing much smaller displacements and much less dissymmetry than those assigned to *d*.

Group *e*.—This group contains lines which are greatly displaced and unsymmetrically broadened towards the violet under pressure.

The lines which are the best suited for standards are those of groups *a* and *b*, which belong to classes 1, 3, and 4. The next best lines are those of group *c*, class 4. St. John and Ware show that the secondary standards which have been adopted belong to the groups *a*, *b*, c_4, c_5, and sub-*d*, and they consider that it would be a gain if all the lines of group sub-*d* were replaced by lines of better quality. The discrepancies that had been noted between the measurements made by different observers in the case of lines of groups *d* and *e* are attributed to the marked unsymmetrical broadening of these lines near the negative pole of the arc. It was this that led St. John and Ware to suggest that the spectrograph slit be placed at right angles to the axis of the arc at the middle point of the enlarged image of the arc. This recommendation has been adopted, as was stated on p. 93.

The Pole Effect.—The unsymmetrical broadening of many of the iron lines near the negative pole, or what is now known as the pole effect, was the subject of an extended investigation by St. John and Babcock.[1] They point out that the measurements by different observers of the wave-lengths of certain iron lines used as standards show discrepancies which far exceed the limit of precision attainable with grating spectrographs, and that the interpretation of displacements as between the sun and arc spectra may be illusory and lead to diverse conclusions, if the presence and influence of certain types of lines are unrecognised. These divergent results depend on the length of the arc, the current density, the portion of the arc used, and they persist in those types of lines which show more or less dissymmetry under varying pressure and line intensity, and have large or abnormal pressure displacements.

The method adopted was to compare under the most rigid conditions of accuracy as possible the spectrum of the arc near the poles with that of the central portion of the arc. Since it was necessary to carry the comparison to the third decimal place in Ångströms, difficulties arose from instrumental causes and observing conditions.

[1] *Astrophys. Journ.*, **42**, 231 (1915).

These were surmounted in a very ingenious manner. A greatly-enlarged image of the arc was thrown on to the slit of a plane grating Littrow spectrograph of 30 feet focus by means of an achromatic lens and a large totally reflecting prism. The light from the central portion of the arc was allowed to enter the slit, whilst by a system of two right-angled prisms the light from any selected portion of the arc was brought on the centre of the slit. The result was that each spectrum photograph consisted of three adjacent spectra, namely, that of the selected portion of the arc situated between two spectra of the central portion. In this way the spectra of the two portions of the arc to be compared were photographed simultaneously.

Now, in making these investigations of relative displacements it is highly desirable that the lines as obtained from the two regions of the arc have as nearly as possible the same intensity in each section of the spectrum photograph. In order to secure this, a rotating sector with variable aperture was placed in the path of the light from the pole of the arc.

The exposures began at the same instant and ended at the same instant, one being continuous and the other intermittent. In this way any effects due to slight temperature changes or instrumental defects resulting from flexure or vibration were effectively eliminated.

There is no question but that many lines show displacements near the pole of the arc, and as these lines show more or less dissymmetry under pressure and are greatly widened at the pole, it might be thought that the displacements are only apparent and arise from the difficulties inherent in the measurement of lines of this character. In order to eliminate as far as possible the disturbing effects due to dissymmetry, St. John and Babcock, as already explained, arranged the net exposure times so as to give practically equal intensities to the lines in the photographs of the two parts of the arc. As the result of this, it was perfectly easy to establish the reality of the displacement and determine its amount. For an extreme case, the relative exposures were so adjusted that the intensity and width of the lines in the spectrum from near the negative pole were less than for the same lines in the spectrum of the centre of the arc. In this case, lines that broaden unsymmetrically could not show in the spectrum of the arc near the pole a displacement which has its origin in this quality of dissymmetry.

Dissymmetry is not evident in the case of every line which is displaced at the pole compared with its position at the centre of the arc. For example, the line at $\lambda = 5339$ is apparently as good a line as the one at $\lambda = 5341$, although the former belongs to group *d* and the latter to group *a*. In the case of one photograph taken as illustration, the width of the former line at the centre of the arc was 0·106 A. and at the negative pole 0·108 A., the displacement being 0·015 A. This displacement cannot be accounted for by an unsymmetrical broadening, when the increase in width is only 0·002 A.

In order to guard against the personal equation of the observer, measurements were also carried out with the Hartmann and the Koch

microphotometers, the latter being a photographic registering instrument. Both instruments proved that the displacements were real, the values being in good agreement with the visual measurements.

Finally, an independent test of the reality of the displacements was made by introducing a vessel of iodine vapour in the path of the rays, so that the absorption spectrum of iodine was superposed on the spectrum of iron. A number of iron lines in the green were found to have iodine lines superimposed more or less centrally upon them. The displacement of the iron lines relatively to the iodine line was seen very clearly in passing from the centre of the arc to the negative pole.

St. John and Babcock discuss in their paper the probable origin of the pole effect, and first consider whether the pressure differs from point to point in the arc by an amount sufficient to account for the observed displacements. They satisfied themselves that no *general* pressure differences occur in the arc. In Table XII. are given data as regards pole effect and pressure shift of lines of groups *a*, *b*, *c*5, *d*, and *e*, the former being expressed as the wave-length at the negative pole *minus* the wave-length at the centre of the arc.

In the lowest row are given the pressure displacements for 1 atmosphere above 760 mm. It will be seen that the displacements of the lines of groups *a* and *b* do not exceed the experimental error, but the pressure effect in the case of the lines of group *b* is of a magnitude to show a change of pressure of one-tenth of an atmosphere, whilst an increase of pressure of $1\frac{1}{2}$ to 2 atmospheres would be required to produce the displacements observed with the lines of groups *c*5 and *d*. On the other hand, the behaviour of the lines of group *e* would indicate a great reduction in pressure.

The possible effects of temperature and density differences were specially investigated by King with his electric furnace,[1] and it was found that neither was sufficient to account for the pole effect. On testing the Pfund arc operated under reduced pressure and under the same conditions as in air, it was found that the pole effect entirely disappeared. The final conclusion reached is that the pole effect is real, but that the explanation of the phenomenon is obscure.

This pole effect was subsequently investigated by Gale and Whitney,[2] and by Whitney,[3] and was further discussed in a later paper by St. John and Babcock,[4] who dealt with the problem of its elimination from the source used for secondary standards of wave-length. It was this work which led to the adoption, in 1922, of the new conditions for operation of the Pfund arc. In this work, St. John and Babcock used interferometric methods as well as the plane grating spectrograph, the apparatus used in the former case being very similar to that of Fabry and Buisson.[5] They succeeded in establishing the marked superiority of the Pfund arc, 12 mm. long, operated with a

[1] See p. 68.
[2] *Astrophys. Journ.*, **43**, 161 (1916).
[3] *Ibid.*, **44**, 65 (1917).
[4] *Ibid.*, **46**, 139 (1917).
[5] See p. 36.

TABLE XII.

Group *a*.		Group *b*.		Group *c*5.		Group *d*.		Group *e*.	
λ.	P − C.	λ.	P − C.	λ.	P − C.	λ.	P − C.	λ.	P − C.
5506	+ 0·0004 A.	6252	0·0000 A.	4957	+ 0·014 A.	5653	+ 0·016 A.	5410	− 0·026 A.
5501	− 0·0004	6230	+ 0·0004	4957	+ 0·014	5393	+ 0·017	5404	− 0·025
5497	− 0·0003	6219	+ 0·0010	4938	+ 0·018	5339	+ 0·019	5383	− 0·025
5341	− 0·0006	6213	+ 0·0003	4920	+ 0·013	5324	+ 0·015	5369	− 0·020
5332	− 0·0002	6137	− 0·0004	4919	+ 0·016	5283	+ 0·018	5367	− 0·025
5328	0·0000	6136	+ 0·0007	4890	+ 0·014	5281	+ 0·019	5364	− 0·028
Mean . . .	− 0·0002 A.	—	+ 0·0003 A.	—	+ 0·015 A.	—	+ 0·018 A.	—	− 0·025 A.
Pressure displacem't	+ 0·0036	—	+ 0·0094	—	+ 0·0094	—	+ 0·0092	—	+ 0·0017

current of 5 amperes or less. The superiority lies not only in the fact that the lines are sharper and give better defined interference fringes, but also in the fact that a central portion about 1·25 mm. long shows no pole effect.

They proved that under the conditions approved in 1913 the Pfund arc exhibits a marked pole effect, even in the central portion, and that

as the result of this some of the adopted wave-length standards are subject to correction for the pole effect. It is also very important to note that the abnormal sun-arc displacements for lines of groups *d* and *e* become of the same order and sign as for stable lines when the pole effect is eliminated. The whole of this work on pole effect has established on a very sure basis the classification of the iron lines first made by Gale and Adams.

Reference may be made to an investigation by Nagaoka [1] to determine whether there is any relationship between the pole effect and the Zeeman effect. Since, according to Gale and Adams, there exists some relation between magnetic separation and pressure-shift for iron, when lines of the same group and the same type of separation are compared, it might reasonably be expected that there would be a connection between the pole effect and magnetic separation. Nagaoka, however, comes to the conclusion that there does not seem to be any direct relation between the two.

Spark Spectra.—The third general method of illumination is by means of the electric spark obtained by the discharge of a high potential electric current from an induction coil or step-up transformer with a condenser in parallel with the spark gap. The sparks are due, of course, to the discharge of the condenser across the spark gap, the condenser being charged to the necessary potential by the current from the induction coil or transformer. The sparks are caused to pass between points or rods of the metal or compound under investigation, or between some conducting substance which carries on its surface the particular compound in question.

Before dealing with the various methods whereby substances may be caused to radiate their characteristic spectra by means of the electric spark, we may consider the electrical apparatus. In the first place, a few words may be said about the use of an induction coil, since careless treatment may readily cause considerable damage to these instruments. An induction coil with a hammer break is a necessary part of the equipment for spectroscopic work, where electric power is not available in the laboratory and the investigator has to obtain his supply of electricity from primary or secondary batteries. The operation of the coil depends on the make and break of the current through the primary coil, this being effected by means of the contact breaker or interrupter. The make and break of this primary current take place between two platinum contacts, one on the interrupter and the other on an adjusting screw. Great care should always be used in adjusting the interrupter so that as little "arcing" as possible takes place when the current is broken, such arcing tending to damage the platinum contacts, and even the coil itself. In all good coils there is provided a tension screw which acts against the lower portion of the spring of the interrupter. It is important that the necessary adjustment of the discharge be made by means of this tension screw and not

[1] *Astrophys. Journ.*, **53**, 329 (1921).

by the adjusting screw carrying the platinum contact. The tension screw should be turned until the spring is entirely free, and then the upper or adjusting screw should be so set that there is about $\frac{1}{32}$-inch clearance between the two platinum contacts. The current is then switched on and the tension screw slowly turned until the required condition of discharge from the secondary is obtained.

With large induction coils where electric power (direct current) is available the hammer break may be replaced by means of a rotating mercury break. If an alternating current is available, then of course this may be used without any form of interrupter. It is, perhaps, not impertinent to point out that every induction coil has a limit beyond which it must not be pushed or the insulation will break down and the instrument ruined.

The design and construction of an induction coil are such as to enable it to give sparks in air, and the size of a coil is indicated by the length of the spark it will give. Thus we find 6-inch, 10-inch, 20-inch, etc., coils, this simply meaning the length of spark in air the coil is capable of giving without danger of breaking down the insulation. This, however, is not what we require in spectroscopy, for what we want our instrument to do is to charge a condenser to a definite potential sufficient to enable the discharge to pass over a gap of a few millimetres. Although the induction coil will serve this purpose, it is not the most efficient instrument possible. It is far better to employ a step-up transformer, of which there are several efficient designs on the market. Since these instruments are not provided with an interrupter, they must be fed with an alternating current. This may be supplied from the laboratory mains if available, or a motor generator driven by direct current may be used.

For work on spark spectra some form of condenser must be used which is connected in parallel with the discharge apparatus. If a condenser be not intercalated in the circuit it will be found that very poor results will be obtained, the discharge being of the nature of a true gaseous discharge. The size of the condenser depends on the size of the induction coil or transformer used, that is to say, a given coil or transformer is only capable of charging up to the necessary potential a condenser of limited capacity. As will be shown in the next chapter, and also in Vol. III., Chapter I., the electric spark discharge tends to excite spectrum lines which are relatively weak in the arc discharge and, indeed, to enhance their intensity. These so-called enhanced or spark lines are due to the ionised atom, that is to say, the atom which has lost one or more of its electrons. We therefore find definite spectra which are due to the singly, doubly, etc., ionised atoms respectively, and in general the stage of ionisation existing depends on the intensity of the spark discharge. In designing an apparatus for the study of spark spectra we have, therefore, to consider the results we wish to achieve. This is, perhaps, a truism, being applicable to every branch of scientific work, but it is legitimate to point out that whatever be the purpose aimed at in the case of spark

spectra, the size of the condenser is the really important matter, and that an induction coil or transformer must be used which is sufficient to charge it to the required potential. It may be assumed that, except in certain cases to be referred to later, the spark length in all work on spark spectra at atmospheric pressure is 5 mm. or thereabouts. The condenser, whatever its capacity, must be charged to a potential sufficient for it to discharge itself across an air gap of 5 mm. or whatever the width of the gap may be. The capacity of the condenser determines the quantity of electricity which passes in each individual spark, that is to say, the intensity of the sparks. The stage of the ionisation present depends on this intensity.

For ordinary work one or two Leyden jars may be used as a condenser, and in this case a medium size induction coil, capable of giving a 4- or 5-inch spark, will be found to be suitable. When a more powerful discharge is required it is advisable to use a plate condenser, which may be made quite readily by interposing sheets of metal between sheets of glass, with every alternate metal sheet connected together. Such a plate condenser may be made by coating both sides of a piece of plate glass with tin-foil, taking care that the tin-foil sheets have a smaller area than that of the glass plate. For example, glass plates 18 inches square may be used and the tin-foil sheets may be 12 inches square, and they are cut with a tongue projecting from one side. In mounting the sheets on the glass plate, the plate is brushed over with a solution of shellac in methylated spirit, and then the tin-foil is carefully laid on to the glass and smoothed out. The two sheets of tin-foil are so mounted that the two tongues project to the opposite sides of the glass plate. Several of such plates may be used, and, if desired, mounted in a wooden frame. A slotted binding screw is fastened to the plates over each tongue, and then one set of binding screws is connected with one pole and the other set with the other pole of the secondary coil of the induction coil or transformer.

The construction of such a plate condenser is considerably simplified by coating only one side of the glass plate with a sheet of tin-foil. In this case the plates are packed in contact with one another, each tin-foil sheet being between two glass plates, and every alternate tin-foil sheet is connected together and to one pole of the transformer. Such a condenser was used by Anderson in his work on the explosion of fine wires and was described above on p. 87. This condenser consisted of 98 sheets of single-strength window glass, 40 × 50 cm., each having a tin-foil coating, 35 × 43 cm., attached with shellac. Again, the tin-foil coating may be replaced by sheets of metal held in position between glass plates by pressure. This device was used by Sawyer (see p. 88), who used sheets of tin-plate, 20 × 25 cm., placed between sheets of double strength window glass 25 × 31 cm. Each unit consisted of 16 tin-plate sheets and 17 glass sheets, and was tightly bound together with cord. The whole condenser was made up out of 16 of these units placed in pairs in large glass accumulator jars and covered with transil oil. With these examples as guide little difficulty will be

found by anyone who wishes to construct a condenser of any capacity for himself.

The capacity of a condenser may be calculated from the formula

$$\frac{KA}{4\pi d}$$

where A is the area in square centimetres of the metal foil or sheets, d their distance apart in centimetres, and K the dielectric constant of glass. For ordinary glass K may be taken as 6. The capacity is usually expressed in microfarads, and in order to express the value obtained from the formula in terms of this unit it must be divided by 100,000.

The next matter which concerns us is the charging of the condenser, and this is one of some importance. In view of the great advance in our knowledge of spark spectra which has been made as the result of the Bohr theory, it is of considerable importance that the details or specification of the spark circuit be given when results obtained therewith are recorded. Unless this is done the real conditions under which those results were obtained will be very obscure. In addition to this it is obvious that there is an element of difficulty arising from the fact that the usual method of charging a condenser by means of an induction coil involves the use of current that is by no means entirely a direct current.

These points have been emphasised by Anderson,[1] who puts forward the following :—

To a rough approximation, when the primary voltage of the current supplied to a high voltage transformer is V the secondary voltage is given by $v = n\mathrm{V}$, where n is the ratio of transformation, and if the primary current is I the secondary current is given by $i = \mathrm{I}/n$. Let this transformer be connected to a condenser of capacity C farads and a standard sphere spark-gap S in parallel, the spark-gap being adjusted to the voltage v. The current in the condenser will be

$$i' = 2\pi \mathrm{NC}v' \quad . \quad . \quad . \quad . \quad (1)$$

if $v' \leqq v$, so that no spark passes across the spark-gap. It follows that when i' is nearly equal to i, as will generally be the case, v' can only equal v if

$$\mathrm{C} \geqq \frac{i}{2\pi \mathrm{N}v} \quad . \quad . \quad . \quad . \quad . \quad (2)$$

To illustrate this we may put C = 0·001 microfarad, which is about the value for a good-sized Leyden jar, and let the required voltage v = 50,000, then if N is 60 cycles we have i = 0·01885 ampere. The size of the transformer required is given by the product of i and v, that is to say, about 950 watts, which means that a transformer of at least 1 kilowatt will be required to charge the Leyden jar to 50,000

[1] *Astrophys. Journ.*, **59**, 76 (1924).

volts on a 60-cycle current. If the capacity of the transformer is less than that value, the potential across the condenser will be less than 50,000 volts. Further, as can be seen from (1), the capacity of the transformer varies as the square of the voltage, and that a 4 kilowatt transformer will be required to charge the condenser up to 100,000 volts.

It will be seen from this that when an ordinary alternating current is used, the size of the transformer, the voltage of the secondary current, and the capacity of the condenser must be known in order to gain even an approximate knowledge of the voltage across the terminals attached to the condenser. It is evident, for example, that a statement to the effect that a 12-inch induction coil was used in connection with a Leyden jar of a certain volume is of little value, and only tells us that the voltage across the spark gap was probably of the order of only a few thousand volts.

We learn from the large size of transformer necessary when operating with alternating current that when a large condenser is used it is necessary to charge it with a unidirectional current which can most conveniently be obtained from a high-power transformer with a suitable rectifying apparatus. The transformer must supply a current which is a little larger than the normal leak of the condenser, and that is practically the only requirement.

In order to determine the instantaneous current when the condenser is discharged, we must know the capacity and voltage of the condenser and the inductance of the circuit. In place of the last, the frequency of the oscillations in the discharge may be used, and this can be measured by photographing the spark with a rotating mirror camera. If this frequency be N_c, and, as before, the capacity of the condenser be C and its voltage v, the maximum value of the current, assuming no damping, will be given by

$$I_c = 2\pi N_c C v \quad . \quad . \quad . \quad . \quad (3)$$

and unless the damping be very great this will be very nearly the maximum value during the first half-cycle of the discharge. With the condenser used by Anderson

$$\begin{aligned} C &= 1 \text{ microfarad}, \\ v &= 20{,}000 \text{ volts}, \\ N_c &= 87{,}000 \end{aligned}$$

and, therefore, $I_c = 10{,}927$ amperes.

If the damping be made critical, which in this apparatus requires the insertion of 2·5 ohms resistance, the maximum value of the current will fall to I_c/e, where e is the base of natural logarithms.

If the inductance L is known, then we can use the well-known relation

$$I_c = v\sqrt{\frac{C}{L}} \quad . \quad . \quad . \quad . \quad . \quad (4)$$

This may be applied to determine the maximum value of the current such as is obtained in ordinary vacuum tube work with the condensed discharge. We may assume a condenser with a capacity of 0·001 microfarad, and a spark-gap in series with the vacuum tube of a few millimetres, so that $v = 5000$. Further, the inductance of an ordinary discharge circuit may be assessed at 0·002 millihenry. Then with

$$C = 1 \times 10^{-9}$$
$$L = 2 \times 10^{-6}$$
$$v = 5000$$

we obtain from (4)

$$I_c = 110 \text{ amperes.}$$

This is remarkably different from the few milliamperes given by the ordinary discharge when no condenser is used.

We may now turn our attention to the spark itself and the various methods which are used to obtain the spark spectra of metals, salts, solutions, etc. In the case of metals the procedure is simple enough, for it is only necessary to use two rods or stout wires of the metal under investigation, which have been filed to a blunt point. These rods or wires may, if desired, be attached to pieces of stout copper wire, the latter being held in some suitable form of clamp. It is very convenient to mount the electrodes in clamps, the position of which can be adjusted during the passage of the spark discharge, so as to enable an image of the discharge to be maintained on the slit of the spectroscope. This arrangement is rendered advisable by the fact that the electrodes burn away during the discharge. Such an apparatus is illustrated in Fig. 42, where the electrodes or the copper wires attached to the electrodes are held in binding screws mounted on insulated supports. Each of these supports can be moved up or down by means of a rack and pinion adjustment.

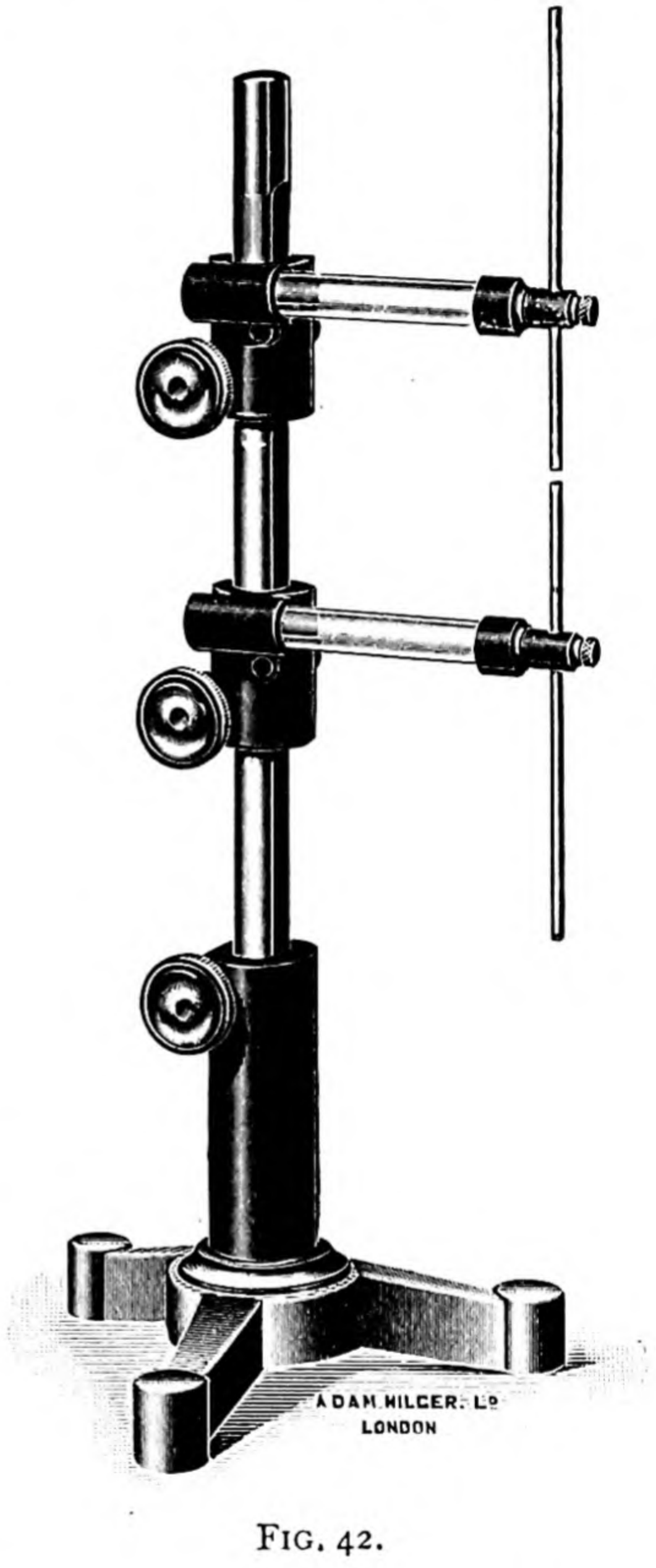


FIG. 42.

In the case of metals, such as cadmium, which burn away fairly

rapidly during the discharge, it is a good plan to use short rods, 5 or 6 mm. in diameter, mounted on stout copper wires. The ends of these rods are filed to a narrow wedge, and when the two electrodes are mounted in the stand, the two wedge-shaped ends are made parallel to one another and to the axis of the spectrograph.

It must not be forgotten that when the spectrum of the spark is examined it will be found that lines are present due to the oxygen and nitrogen of the atmosphere. The relative intensity of these air lines is, in general, inversely proportional to the volatility of the metal composing the electrodes. It is, of course, necessary in any work on spark spectra to eliminate these lines, and this may be done by comparing photographs of two spark spectra when the lines common to both will be the air lines. The best comparison spectrum to use is that of the spark between platinum electrodes, in which the air lines have a relatively high intensity.

It was shown by Hemsalech [1] and by Schuster and Hemsalech [2] that if a self-induction coil is introduced into the spark circuit the air lines disappear. A self-induction coil can be made quite readily by winding stout copper wire round a bobbin. The coil used by Hemsalech in some of his experiments was 50 cm. long, 5 cm. internal diameter, and contained 8 layers of wire, each consisting of 150 turns. The work of these experimenters on the mechanism of the spark may be discussed below.

The presence of the air lines in a spark spectrum is not necessarily a disadvantage, since the wave-lengths are known, and consequently they may be used as standards in an approximate determination of the wave-lengths of unknown lines. Again, in the comparison of the spark spectra of two sources the presence of the air lines in the two serves as a means of testing whether the two are correctly oriented.

The spark spectrum of a metal such as cadmium is an admirable source of rays for use in many physical measurements, such as the refractive indices of liquids and solids, the refractivity of gases, etc. In many respects the spark discharge has considerable advantages over the arc discharge, such, for example, as the readiness with which it may be started and stopped without any adjustment being necessary in its orientation with respect to the observing instrument.

If the spectra are required of metals which cannot readily be obtained in the free state, for example, molybdenum, vanadium, uranium, etc., these may be observed by passing the spark discharge between pure carbon cones which have previously been saturated with a salt of the metal. This method was first used by Bunsen,[3] who employed small cones of wood charcoal which had been treated in the following way: The cones were freed from impurities by first of all heating them at a white heat when surrounded with powdered charcoal, and then by boiling them successively with hydrofluoric,

[1] *Comptes Rendus*, **122**, 285 (1899). [2] *Phil. Trans.*, A. **193**, 189 (1900).
[3] *Phil. Mag.*, **50**, 417. 527 (1875).

nitric, and hydrochloric acids, care being taken to wash them thoroughly with water after each treatment. The cones were then dried and boiled in an aqueous solution of the required metallic salt. If available, the nitrate is the most suitable salt to use, since after treatment with this salt the cones are heated at a red heat and the oxide will be obtained. In this case the treatment with the solution and subsequent heating may be repeated several times. If the nitrate is not available, then any convenient salt may be used, and, particularly if the metal gives an acid-forming oxide, the ammonium salt of that acid may be employed. As an example of the latter type of salt is ammonium molybdate, and carbon poles may readily be thoroughly impregnated with molybdenum oxide by the above treatment.[1] Owing to the fact that these carbon poles burn away fairly rapidly during the passage of the spark discharge, it is advisable to file their ends, not to a point, but to a wedge, as was mentioned above in the case of the more easily oxidised metals.

Reference has already been made to the use in absorption spectra observations of a source the spectrum of which is very rich in lines. H. C. Jones, in his investigations in this field, used carbon electrodes which had been thoroughly impregnated with uranium and molybdenum oxides. The electrodes were first boiled in a concentrated solution of uranyl nitrate, dried and heated to dull redness, this process being repeated three times. They were then boiled in a concentrated solution of ammonium molybdate, dried, and heated to a dull redness, this process also being repeated three times. The spark spectrum given by these electrodes is extremely rich in lines which are very evenly distributed and do not vary greatly in their intensities.

The spark spectrum of any mineral, which possesses sufficient electrical conductivity, can also be obtained. It is then convenient to pass the discharge between two fragments of the mineral held in spring clips which are mounted on thin rods held in any convenient form of stand. An extended study of the spark spectra of minerals was made by de Gramont, who was not only able to determine thereby the metals present, but was also able to estimate the amounts to a very close approximation. The application of quantitative methods to spark spectra will be dealt with below on p. 124.

We may next consider the spark spectra of solutions, and many methods have been used for this purpose, and of these the following may be selected: Two pieces of apparatus are shown in Fig. 43 at *a* and *b*; the design *a* is due to E. Becquerel,[2] and the design *b* to Delachanal and Mermet.[3] In both cases platinum wires are used, and the solution of the salt is always made the negative pole. In *a* the discharge passes between the positive platinum wire and the

[1] It may be pointed out that there can now be obtained commercially carbon rods which have been very carefully purified. These are made by the General Electric Company at Birmingham, and are sold by Adam Hilger, Ltd., London.

[2] *Comptes Rendus*, **65**, 1097 (1867); **66**, 121 (1868).

[3] *Ibid.*, **81**, 766 (1875).

solution, whereas in *b* the negative platinum wire is kept wetted by the solution, which ascends by capillary attraction inside the small glass cone.

In Fig. 44 is shown an apparatus which was used by Hartley [1] in much of his extended work on spark spectra. The two electrodes are made of graphite and are cut to a chisel shape. The lower elec-

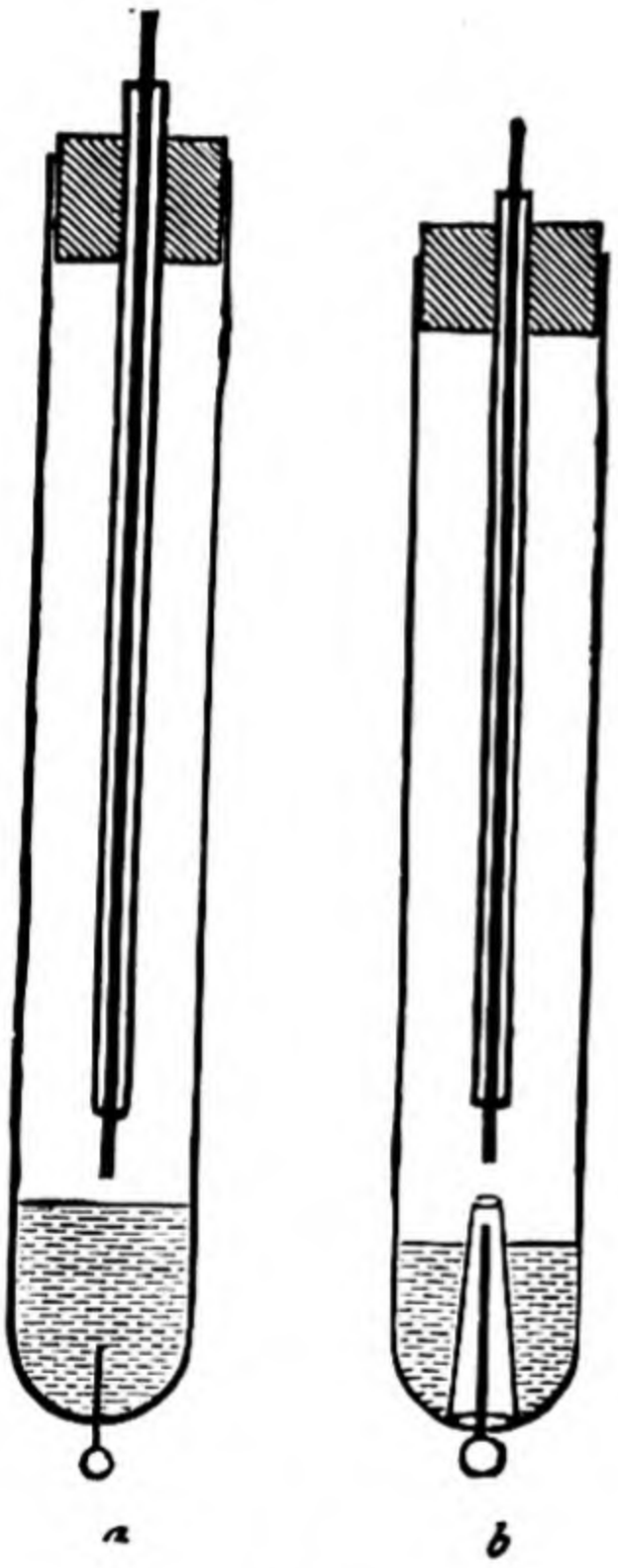


FIG. 43.

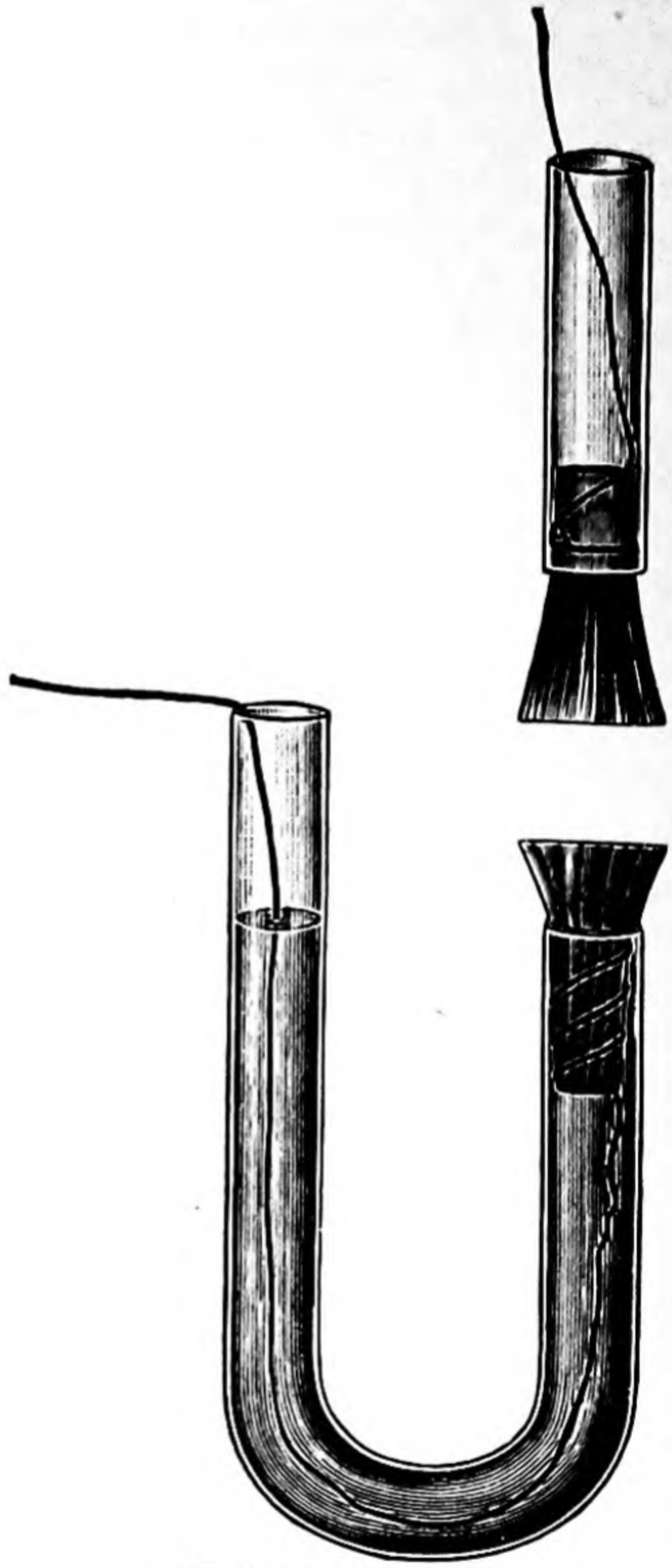


FIG. 44.

trode has grooves cut in it, and is placed in a U-tube filled with the salt solution, which ascends through the grooves by capillary attraction. The lower electrode is made the negative, and, as previously mentioned, the wedge-shaped ends are set parallel to one another and to the axis of the collimator tube of the spectrograph, so that the wandering of the spark along the chisel edges causes no displacement

[1] *Phil. Trans.*, 175, 49 (1884).

of the image thrown on to the slit. This apparatus possesses one advantage over the first two described in that there is no containing wall to exercise its absorptive power on the rays emitted by the discharge.

A somewhat similar apparatus, in which the graphite wedges are replaced by gold wire, was designed by Pollok for obtaining the spark spectra of solutions under standardised conditions, such as are required when quantitative methods are applied. This apparatus is illustrated in Fig. 48 on p. 135 below.

A very convenient method of obtaining the spark spectrum of solutions has been used by de Gramont.[1] The spark is passed between two drops of the solution, one above the other, at the ends of two capillary tubes of fused silica. A successful trial has also been made by Errera [2] of colloidal supports for the solution to be examined. The colloidal material used is gelose, which is a carbohydrate contained in agar-agar, and also occurs in the plants of the *Gelidium* species. The gelose is first of all purified from inorganic salts by dialysis, the material being kept in a slow stream of distilled water for a week. The removal of the salts may be hastened by occasionally squeezing the gelose like a sponge. After this purification the gelose is placed in a flat dish with sufficient water to form a 4 per cent. solution, calculated on the dry material, and the whole is heated at 120° in an autoclave for about ten minutes. On cooling a stiff white jelly is obtained. From this jelly rods about 7 mm. in diameter and 50 mm. long are cut by means of a cutting press, and these rods are placed in the required salt solution and allowed to remain during some hours. At the end of this period the rods are thoroughly impregnated with the salt, and they then can be mounted on brass supports which are connected to the condensed spark circuit.

The method is very satisfactory. When the gelose rods are sparked without any previous treatment with a salt solution the spectrum shows certain lines which, however, decrease in intensity the longer the period of dialysis. The following lines are observed after long exposures :—

Silver	$\lambda = 3383{\cdot}0,\ 3280{\cdot}7$
Calcium	$\lambda = 4226{\cdot}7,\ 3968{\cdot}5,\ 3933{\cdot}7$
Magnesium	$\lambda = 2852{\cdot}1,\ 2802{\cdot}7,\ 2795{\cdot}5$
Copper	$\lambda = 3274{\cdot}0,\ 3247{\cdot}5$
Sodium	$\lambda = 3303$ (mean of pair).

In addition to these there appear the water bands at $\lambda = 3089$, 3067, 3064, and the air lines at $\lambda = 3577$, 3536, 3371, and 3159. This method is very suitable for analytical work by the use of the ultimate rays.[3]

Two simple pieces of apparatus have been described by Krulla [4] for obtaining the spark spectra of metallic salts in solution. The

[1] *Comptes Rendus*, **145**, 1107 (1907).
[2] *Ibid.*, **176**, 1874 (1923).
[3] See p. 148.
[4] *Zeitschr. phys. Chem.*, **66**, 78 (1909).

essential feature of the design is that the discharge passes between two surfaces of the solution. The two apparatus are shown in Figs. 45 and 46, and in the former the salt solution is placed in the tap-funnel and in the U-tube, connection being made with the sparking circuit by means of platinum wires sealed through the glass, as shown. The stopcock is opened sufficiently to obtain a jet of the solution, which breaks into drops just above the surface of the solution in the U-tube. The discharge passes between the dropping stream and the lower liquid surface, and, though it flickers considerably, the source of light is very intense.

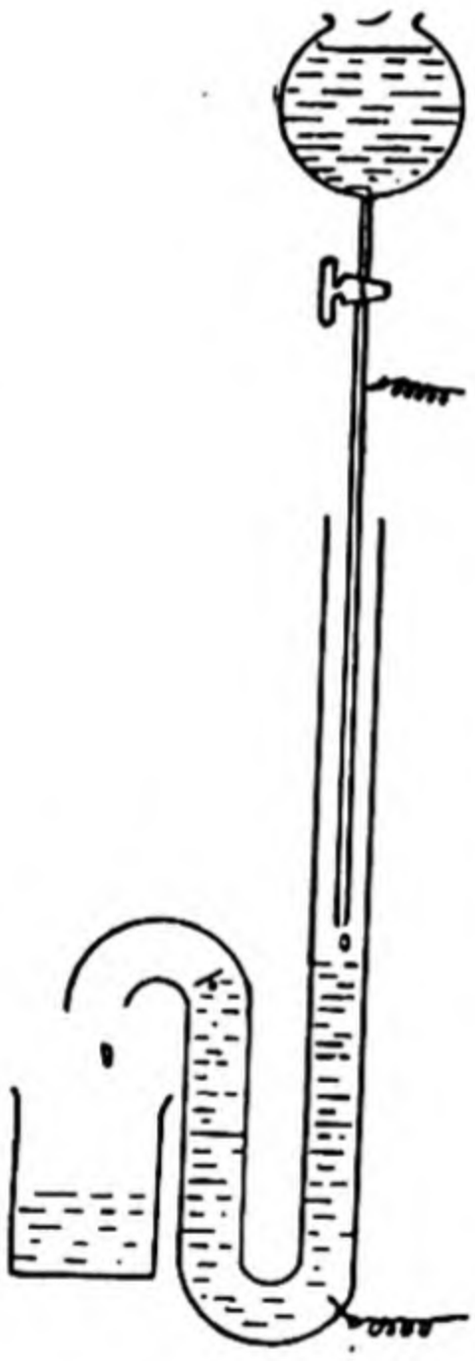


FIG. 45.

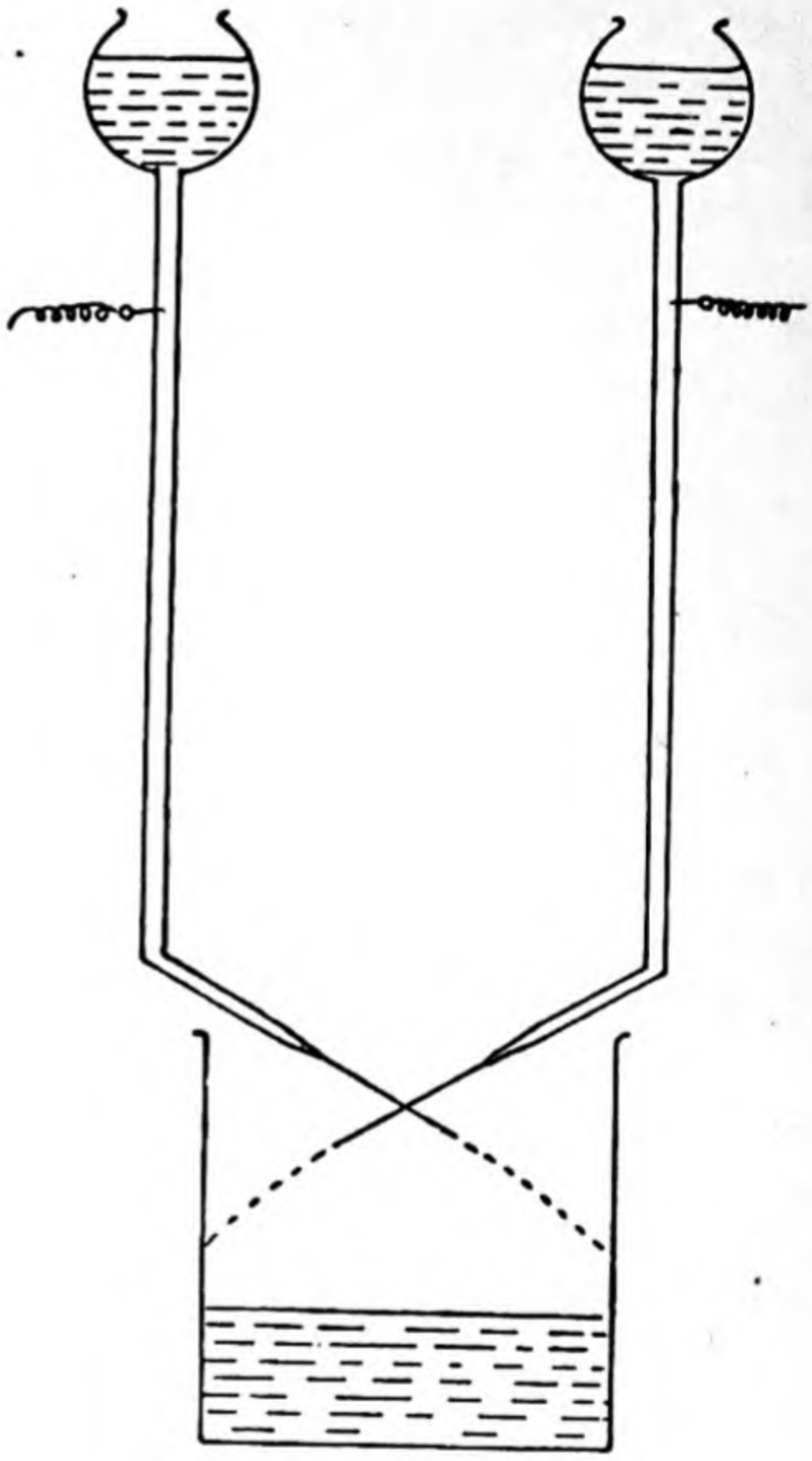


FIG. 46.

The second apparatus is more advantageous, but it requires a larger volume of solution. As shown in Fig. 46, there are two funnels, the lower tubes of which are bent and drawn out so as to deliver fine jets of liquid. A platinum wire is sealed into each funnel and these wires are connected to the sparking circuit. Both funnels are filled with the solution, and they are so adjusted that the two jets pass within 2 mm. of one another at some point, care being taken that the jets do not break up into drops before this point. When the sparking circuit is completed the discharge passes at this point and is very brilliant and perfectly steady.

As already stated, Hartley [1] carried out an exhaustive study of the spark spectra of substances, and his conclusions on the spark spectra of metals and their salts may be given very briefly.

In the case of carbon or metallic electrodes, when these are moistened with water, the short lines are lengthened.[2]

With very few exceptions the non-metallic constituents of salts do not affect the spark spectra of solutions.

Insoluble and non-volatile compounds do not yield spark spectra.

Solutions of metallic chlorides give spectrum lines which are identical in number and position with the principal lines of the metals.

Short lines become long, but otherwise their character is identical whether the spectra are produced by metallic electrodes or solutions of the salts.

The effect of dilution solutions of metallic salts is first to weaken and attenuate the lines, then, with further dilution, to shorten them, the length of the longest and strongest lines generally decreasing until they finally disappear.

The last-mentioned observation of Hartley's is of considerable importance, since he showed that all the lines of a given spark spectrum do not disappear at the same dilution. Indeed, the lines may be divided into groups, each group having a specific persistence as the concentration of the salt is decreased, and disappearing when a certain lower limit of concentration is reached. It is on this phenomenon that the quantitative method of estimation has been based, which has been applied with such success by de Gramont and others.

Reference may be made here to a very interesting set of observations by Goldstein,[3] who has described a new method of obtaining the spark spectra of both metals and non-metals.

A vertical glass tube is taken which has an electrode at each end, and a quantity of a well-powdered and perfectly dry alkali metal halogen salt is put into it. Sufficient of the salt is taken completely to cover the bottom electrode, which is made the anode. The tube is then exhausted, and when the discharge is passed it always follows a path between the salt and the glass walls of the tube. The discharge is intensely brilliant, and if no condenser is used in parallel with the tube, the spectrum is always that of the alkali metal, while if a condenser is used the spectrum of the halogen (chlorine, bromine, or iodine) is seen. Goldstein has also succeeded in this way in observing the spectra of sulphur, arsenic, phosphorus, antimony, and silicon. When potassium fluoride was used with the condensed spark a new spectrum of potassium was obtained, the spectra of fluorine being too weak to have any influence. The corresponding spectra of rubidium and cæsium were also observed in the same way, and Goldstein gave the name of fundamental spectra to them. He subsequently found that the same spectra were given when the condensed spark was

[1] *Phil. Trans.*, **175**, 49 (1884). [2] See Chapter III., p. 196.

[3] *Ann. der Phys.*, **27**, 773 (1908); *Verh. d. Deutsch. Phys. Gesell.*, **10**, 426 (1910), and also *Phys. Zeitschr.*, **11**, 560 (1910).

passed through the vapours of the three metals. We now know that these fundamental spectra are really the enhanced spectra of these metals, that is to say, the spectra of ionised potassium, rubidium, and cæsium.

The Electric Spark in a Vacuum.—In the work carried out by Millikan and others on the extension of emission spectra into the region of very short wave-lengths, described in Vol. I., p. 272, a very important factor was the excitation of the element sufficiently to radiate in that region. It is obvious that in any work with vacuum spectrographs no absorbing material can be employed, and, therefore, the source must be operated within the highly exhausted apparatus. Whilst it is well known that the electric arc may be used in a vacuum, as indeed was used by Saunders in his work on spectral series,[1] the radiation does not extend beyond the limit of about 950 A. The problem was solved by the use of the electric sparks produced by the passage of a powerful condensed discharge between electrodes of the element under investigation placed very close together and connected in series with an adjustable spark gap in air. These vacuum sparks were observed by Rowland[2] and by Wood,[3] and the nature of the discharge was investigated by Loving.[4] The standardisation of these sparks as a source of radiation in the extreme ultra-violet was carried out by Millikan.[5] A comparison of the spectra given between $\lambda = 6600$ and $\lambda = 4000$ by these sparks and by the ordinary spark in air was made by Miss Carter.[6] A detailed account of the method of operating these sparks has been published by Sawyer.[7]

The apparatus used for these sparks depends upon the uses to which the light is put, but is simple enough in any case. In Millikan and Sawyer's work with the vacuum spectrograph the two electrodes were placed immediately in front of the slit, both being situated inside the exhausted apparatus. In other work they may be mounted in a glass vessel provided with a suitable window. In either case one of the electrodes at any rate must be capable of movement so that the spark length may be adjusted.

A very powerful condensed discharge must be employed, and for this Miss Carter used a large industrial coil with an electrolytic interrupter fed with 15 to 20 amperes. The condenser consisted of copper plates, 56 × 61 cm., separated by glass plates 5 mm. thick, the whole being immersed in oil. The Pasadena equipment consisted of a large induction coil (10-inch spark) fed with alternating current at 110 volts with 60 cycles. The condenser was made up of four large Leyden jars.

The air spark gap must also be adjustable in length and Sawyer

[1] *Astrophys. Journ.*, **40**, 377 (1914).
[2] *Physical Papers*, p 574.
[3] *Phys. Rev.*, **5**, 1 (1897).
[4] *Astrophys. Journ*, **22**, 285 (1905).
[5] *Ibid.*, **52**, 47, 286 (1920); **53**, 150 (1921); *Phys. Rev.*, **12**, 168 (1918); **15**, 239 (1920); *Science*, **19**, 138 (1919).
[6] *Astrophys. Journ.*, **55**, 162 (1922).
[7] *Ibid.*, **52**, 286 (1920).

says that with his apparatus, using zinc electrodes, this spark gap was about 1 cm. at the commencement of an exposure. Owing to the fatigue effect the resistance of the vacuum spark gap increases so that the external gap must be reduced until it is finally closed up. The length of the vacuum spark gap depends on the electrodes, and lies between 0·01 mm. and 0·2 mm. There is always a tendency for gases to be evolved during the sparking, and these cause the discharge to pass over into the ordinary form of gas discharge, and the result is that only a few sparks can be passed, and then some time must elapse during which the evolved gases are pumped off, the pump being kept in operation during the whole process. The following description may be quoted from Sawyer's paper, and refers to the photographing of the spectrum of these sparks with the vacuum spectrograph, it being assumed that the apparatus has been completely exhausted. On throwing on the potential a little greenish glow was observed round the electrodes. There was no general glow, however, and most of the discharge passed between the electrodes in the form of a brilliant spark, bluish-white in colour in the case of zinc. This discharge would so heat the electrodes, conductors, and insulation that a considerable quantity of gas would be thrown out. After the passage of three or four series of sparks, of perhaps one second in duration, the pressure in the spectrograph would be so raised by the evolved gases that the discharge would tend to become wholly gaseous. This was not allowed to happen, for the pumps would remove the gases in a few minutes and the process could then be repeated. After a number of such series of sparks the evolved gases would be much reduced and the hot sparks became much stronger. Five or ten brilliant series of sparks of one second's duration could then be obtained at intervals of about five minutes. These intervals were necessary to allow the pumps to remove the gases which were always thrown off to some extent by the electrodes. The number of such spark series required to complete an exposure depended on the brilliancy of individual series of sparks; generally from 150 to 250 were required. As the duration of an individual series of sparks was approximately one second, it will be seen that the total period of actual exposure was not more than 15 or 20 minutes in length. Perhaps this fact, more clearly than any other, will indicate the brilliancy of the sparks obtained by this method.

The hot spark obtained with zinc electrodes was bluish-white in colour and very much resembled the ordinary spark in air. After a few poor sparks at the beginning of an exposure, the sparks obtained a maximum of brilliancy, which gradually fell away as the fatigue effect became operative. This effect became more and more pronounced and made the sparks more and more difficult to produce. The electrodes spattered badly and their tips began to present a rough and fused appearance.

Sawyer concludes by saying that the fatigue effect in some instances actually imposed a limit on the length of the exposure, so

difficult did it become to persuade the spark to pass across the gap, even when this was reduced to 0·1 mm.

With reference to Sawyer's statement that the appearance of the vacuum spark between zinc electrodes is very similar to that in air, mention may be made of Miss Carter's observations with calcium, magnesium, cadmium, titanium, and iron. She found that with calcium and magnesium the spectra given by the spark in vacuo and in air are practically identical. In the case of cadmium the arc lines have a greater relative intensity in the vacuum spark than in the ordinary spark, and this effect is still more pronounced with titanium. In spite of that the vacuum spark spectrum of titanium is plainly an enhanced spectrum, as is evidenced, for instance, by the intensity of the enhanced lines at $\lambda = 4172$ and 4164.

On the other hand, the vacuum spark spectrum of iron resembles the arc spectrum more closely. The low temperature arc lines are missing, and the lines which are stronger at the poles and in the core of the arc are relatively more intense in the vacuum spark spectrum. Some enhanced lines are, however, present, such, for example, as $\lambda = 5316$, 5018, 4515, and 4508.

The vacuum spark has been utilised by Sawyer and Paton [1] in a study of the spark spectrum of silicon. The current was supplied by a 100,000-volt closed core transformer fed at 110 volts. The condenser had a capacity of about 0·01 microfarad. Pure elementary silicon was used as electrodes, the maximum spark length being 1 mm. The electrodes were heated white-hot almost instantaneously, and some of the silicon was volatilised, this causing the fogging of the window of the discharge chamber. The exhaustion of this chamber was carried to as high a point as possible by two mercury vapour diffusion pumps in series together with an oil pump. A trap cooled in liquid air was introduced between the mercury vapour pumps and the discharge chamber to remove any vapour such as those of water and mercury. The pressure reached was of the order of 0·0001 mm. of mercury. In order to guard against the troubles introduced by the heating of the electrodes, such as the evolution of gases, a rotating commutator switch was introduced into the primary circuit of the transformer, and this switch was so adjusted that the current was turned on forty times a minute for about half a second at a time.

The vacuum spark spectrum of calcium has been investigated by Anderson,[2] who used the condenser constructed by him for his work on the explosion of thin metallic wires.[3] This condenser has a capacity of about 1 microfarad and is capable of being charged to a potential of 20,000 volts. The condenser was charged through a synchronous rectifier from the secondary of a 0·5 kilowatt transformer giving 26,000 volts. It took 4 to 5 seconds fully to charge the condenser up to 20,000 volts as measured by a 6-inch sharp gap in air, the charging current falling during that period from about

[1] *Astrophys. Journ.*, 57, 279 (1923). [2] *Ibid.*, 59, 76 (1924).
[3] See p. 86.

20 milliamperes to a very small value at the end of 4 seconds. The condenser was discharged by closing a 3-cm. spark gap in series with the vacuum spark. The current passing across the vacuum spark gap was thus always the same, the maximum value in the first half-cycle being of the order of 10,000 amperes. The potential difference between the electrodes, however, depended upon the voltage drop across the external spark gap. It could never exceed 20,000 volts, and, in general, was much less.

The discharge chamber consisted of a glass bulb, the electrodes being mounted through two side tubes attached on opposite sides of the bulb. A third tube several inches long, with a quartz window cemented at the end, allowed the rays to pass to the spectrograph slit.

Anderson describes the changes in the nature and appearance of the sparks as the pressure is reduced in the discharge chamber. At pressures from 76 down to 10 or 15 cm. these powerful sparks resemble the ordinary condensed spark, except that they are rather broad. On reducing the pressure to a few millimetres, the spark expands to a remarkable extent, the intensity falling in the vicinity of the electrodes so that at 1·0 to 0·1 mm. pressure it is not much greater between the electrodes than at other places in the bulb. With further decrease in pressure, an exceedingly bright layer appears on each electrode, and at still lower pressures this layer increases in size until it completely fills the gap between the electrodes. At this stage there is only a relatively feeble glow through the rest of the bulb. No further change occurs when the pressure is diminished until the stage is reached when no discharge whatever can be made to pass.

Owing to the power possessed by certain metals of combining with oxygen and nitrogen, it was found that when the electrodes were made of calcium, zinc, or aluminium they became so hot with one spark every 5 seconds that the pressure was reduced too low for further discharges to pass. After a short time sufficient gas diffused back from the pump, which was a Cenco rotary oil pump, to raise the pressure above the critical limit. This effect was not observed when the electrodes were made of magnesium, iron, copper, or lead.

In the investigation under review calcium electrodes, 6 mm. in diameter, were used, and the distance between them was 2 mm. It is of considerable interest that 850 lines between $\lambda = 6499{\cdot}70$ and $\lambda = 2081{\cdot}47$ were observed, which seem to have their origin in the calcium atom, and of these the total number previously known is 46. In all probability there are present in this spark spectrum many lines due to doubly ionised calcium atoms Ca^{++}, as well as those of the singly-ionised Ca^{+}.

Anderson bases the intensities which he gives to the lines on a scale of exposures which were made in geometric progression. Separate photographs were taken of the spectra given by 400, 100, 25, 6, and, in a few cases, 2 sparks. Then a line which is just nicely visible in the 6-spark spectrum is given the intensity 6, a line just visible in

the 25-spark spectrum is given the intensity 4, lines just visible in the 100-spark and 400-spark spectra are given the intensities 2 and 0 respectively. A line which is easy to see in the 400-spark spectrum, and is not measurable in the 100-spark spectrum, is given the intensity 1, and so on.

The Arc and Spark Discharge in Liquids.—Important and interesting work has been carried out in the way of electric discharges under the surfaces of liquids, both arc and spark discharge having been investigated. That the electric arc could be made to burn under water was first noticed by Humphry Davy[1] in 1802; Masson,[2] in 1851, experimented with the arc under different liquids, but only found a continuous spectrum. Liveing and Dewar,[3] using carbon poles under water, observed the bands of the Swan spectrum, but none of the cyanogen bands, even though the water contained ammonia or potassium nitrate. An investigation has been carried out by Konen[4] on the spectra obtained by burning the arc with poles of various substances under various liquids. For the maintenance of the arc a continuous current was used of 60 amperes at 72 volts, or 20 amperes at 220 volts, and the electrodes were placed in a deep glass basin with a quartz window. A quartz lens focussed the rays upon the slit of a spectroscope with a grating of 1 metre focus. For the electrodes copper, iron, brass, or carbon was used, and a great many liquids were tried. A great deal of trouble was met with, because the electrodes rapidly disintegrated, except in the cases of organic liquids, when graphitic carbon was deposited upon them. The liquid was in this way rendered muddy very quickly, but this difficulty was overcome by having a tube, open at both ends, reaching from the arc to the quartz window; into this tube by a side branch fresh liquid was continuously supplied. In all cases a continuous background to the spectrum was obtained, reaching to $\lambda = 3600$, while certain metallic lines were seen, namely, the calcium lines at $\lambda = 3634$ and 3969, and also the aluminium lines at $\lambda = 3944$ and 3962; the D lines of sodium were also present, but always as absorption lines. The following metallic spectra were examined: iron, copper, and brass, also calcium, barium, sodium, potassium, lithium, and thallium, and these all gave bright line spectra. In no case were any banded spectra seen. The lines generally were sharper than in the case of the arc in air, their intensity less, and there were fewer self-reversals, so that this method is to be recommended for the study of metallic spectra. The nature of the surrounding liquid has no influence upon metallic spectra, except in cases of certain concentrated salt solutions of the metals barium and calcium, when the strongest lines of the dissolved metals make their appearance. The metallic spectra can, however, be obtained if cored carbons containing metallic salts be used.

In the case of carbon electrodes the surrounding liquid has, of course, a great influence. Under ordinary circumstances, in the

[1] *Journ. Roy. Inst.*, 1, 165 (1802).
[2] *Ann. Chim. et Phys.*, 31, 295 (1851).
[3] *Proc. Roy. Soc.*, 34, 123 (1882).
[4] *Ann. der Phys.*, 4, 742 (1902).

carbon arc the four cyanogen bands are obtained, with their heads at $\lambda = 4606{\cdot}33$, $4216{\cdot}12$, $3883{\cdot}55$, and $3590{\cdot}48$, but if the carbon rods are well heated first and then the arc is made in water which has been previously well boiled, these four bands are invisible, and only the Swan bands can be seen. A very small quantity of air blown into the water at once gives the cyanogen bands; their invariable absence when no nitrogen is present in the liquid and their appearance in the presence of nitrogen conclusively proves the origin of these bands to be cyanogen.

As regards the spark of discharge in liquids, Wilsing[1] was the first who obtained any practical results in this direction; he employed electrodes of different metals, and made the spark from a large induction coil to pass between them under water. A spark gap with electrodes of the same metal was placed in series, and photographs of the two spectra were simultaneously taken upon the same plate. He found that in the case of the spark under water considerable broadening and shifting of the lines to the red took place, also a considerable number of reversals. Wilsing explained the shifting of the lines as being due to the pressure effect as investigated by Humphreys and Mohler;[2] the actual effects he obtained varied from 6 A.U. with zinc to 1 A.U. with iron, and nothing with platinum.

Hale,[3] in 1902, investigated the particular case of iron electrodes in water and salt solutions, and found that a part of the iron spectrum was reversed; further, that the reversals tend to increase in number and intensity with (1) the length of the auxiliary spark gap in air (placed in series with the spark in water); (2) the diameter of the electrodes; (3) the capacity of the condenser; (4) the pressure of the water; (5) the strength of the solution in salt solutions. With a 9·5 per cent. solution of barium chloride almost all the spectrum can be reversed; certain shiftings of the lines were observed also in certain groups. Lockyer[4] also made investigations in the same field, using various metals as electrodes in pure water. Iron, zinc, magnesium, silver, lead, and copper electrodes were tried, but only the first three showed any reversals. The phenomenon noticed may be divided into three classes: (1) broadened bright lines, well shown in the copper spectrum, the lines being stronger on the blue side and hazy towards the red; (2) broadened bright lines, with central absorption well shown by line at $\lambda = 4063{\cdot}76$ in the iron spectrum; (3) broadened bright lines, with non-symmetrical absorption (maximum of emission towards the red), also best shown by several iron lines.

Konen[5] in his paper gives the results of a series of observations he has made with many metals in a great number of liquids. He investigated the brush discharge and also the condensed and uncondensed spark discharge, using a coil capable of giving a spark of one

[1] *Berl. Ber.*, 426 (1899); and *Astrophys. Journ.*, **10**, 113 (1899).
[2] *Ibid.*, **3**, 114 (1896).
[3] *Ibid.*, **15**, 132 (1902).
[4] *Proc. Roy. Soc.*, **70**, 31 (1902); and *Astrophys. Journ.*, **15**, 190 (1902).
[5] *Loc. cit.*

metre long in air. The brush discharge was found to be too faint to be spectroscopically investigated, whilst the uncondensed spark gave weak lines upon a continuous background; the latter gave the Swan spectrum in carbon containing liquids. When a condenser was intercalated in the secondary circuit the whole effect was altered; the intensity of the continuous spectrum was increased, it being possible with two carbon electrodes to get it absolutely continuous. The surrounding liquid has just as little influence as in the case of the fluid-enclosed arc. As regards reversals, Konen was not able to repeat Hale's results with the solutions of salts, and in the case of a 9·5 per cent. barium chloride solution no reversal was seen; there is thus a considerable difference between the effect of the discharge produced by an alternating current as in Hale's case, and one from an induction coil. Konen, however, agreed with Wilsing's results, for he found bright and dark lines together, and was not able to obtain all the lines bright or all reversed. Konen considered that Lockyer's reversals were nearly all self-reversals, as they were dark lines on a bright ground, whilst the truly reversed line is black upon a faint continuous background; Lockyer's results, therefore, must be due to a different phenomenon. Konen also observed a shifting of the lines towards the red comparable with that found by Wilsing; in the ultra-violet from $\lambda = 2755$ to $\lambda = 2606$ the lines were displaced about 2 A.U. towards the red; with lines of greater wave-length the shift was less.

Some further very important work has been carried out on this subject by Konen [1] and by Finger,[2] who examined the spark spectra of more than 17 metals under water, and the results given by a comparison of the water-spark spectra and the air-spark spectra are very complex. Certain differences between the two were noted which may be mentioned. In the first place, the change from the spark in air to the spark in water does not give the same results as an increase of pressure does on the spark in air. The following changes in the character of the various spectrum lines on passing from air to water were recognised: reversal, broadening, strengthening, weakening loss of definition, change in wave-length, and entire disappearance. The most important result obtained in this work is that all the lines belonging to the same series in any one spectrum undergo the same change. Besides the lines which unmistakably belong to the series, there are other lines which are usually grouped together for some definite reason, as, for example, the enhanced lines. The behaviour of these lines is of considerable interest, but very few regularities could be detected amongst them as regards their behaviour when the spark is changed from air to water. For example, it would appear that the enhanced lines in any one spectrum do not necessarily behave in exactly the same way. In many cases an increase in the intensity is to be noticed, but no general regularity in this increase is

[1] *Zeitschr. Elektrochem.*, **15**, 165 (1909). *Verh. d. Deutsch. Phys. Gesell.*, **11**, 369 (1909).

[2] *Zeitschr. wiss. Phot.*, **7**, 329 and 369 (1909).

evident. The authors came to the conclusion that the difference in the behaviour of the enhanced lines in a spectrum under the same conditions of emission justified them in concluding that these lines have not one common origin, but that they arise from different conditions. For this reason they felt that it was not possible to attribute, with Lockyer, such lines to one special line spectrum. The explanation of this view is doubtless to be found in the fact that in the case of the very powerful condensed discharge used by Konen and Finger enhanced lines were observed which arose from more than one stage of ionisation, that is to say, two or possibly more enhanced line spectra were superposed.

The electric spark under water has been used with great success in work on absorption spectra, where a continuous spectrum extending into the far ultra-violet is essential for the study of the fine line structure of absorption bands. As an instance of this the apparatus used by Henri and de Làszlò may be mentioned,[1] and this is diagrammatically shown in Fig. 47, which has been copied from their paper. C_1 and C_2 are two condensers, each having a capacity of

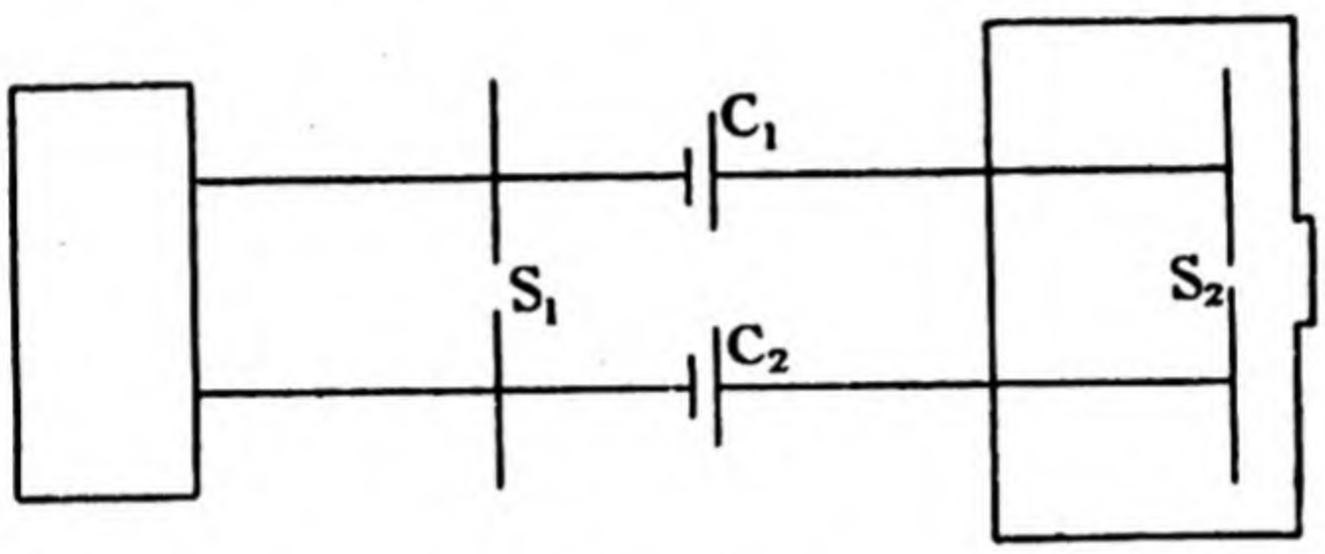


FIG. 47.

$2{\cdot}3 \times 10^{-3}$ microfarad, which are connected in parallel. S_1 is a spark-gap with a spark length of from 15 to 20 mm., and S_2 is the water spark between two firmly mounted electrodes, 8 mm. in diameter, the distance apart of which can be accurately adjusted by means of a micrometer screw. The transformer is supplied with a primary current of 20 amperes at 60 volts, interrupted 600 times a second. The tank for the water spark is made of teak, and holds three litres of distilled water. The spark takes place 5 cm. below the surface of the water and at a distance from 10 to 15 mm. from the quartz window. All the connections are made of copper wire and are led as straight as possible in order to reduce the self-induction to a minimum, this being a most important feature of the circuit. The frequency of the oscillatory discharge was measured and found to be of the order of one million per second.

The spark given by this is fairly uniform and very intense, an exposure of 3 to 5 minutes giving a continuous spectrum reaching from the visible region to $\lambda = 2100$ A. Both aluminium and copper electrodes may be used.

[1] *Proc. Roy. Soc.*, A, **105**, 662 (1924).

Enhanced Lines.—A very important feature of spark spectra is the enhancement of the intensity of certain lines in the spectra of elements when the spark discharge is substituted for the arc discharge. Lockyer was the first to draw attention to this phenomenon and to point out its great significance. It was Lockyer, too, who first discovered that many of these enhanced lines appear in certain stellar spectra. The earlier results obtained by Lockyer in the course of his experiments were published in 1879 [1] and 1881,[2] and the development of his theory based on subsequent work [3] is of more than passing interest in spite of the fact that the Bohr theory has supplied the key to the problem of the actual origin of these lines.

The development of the subject of spectroscopy and atomic physics during the last twelve years or so has been truly remarkable, and there is little doubt that any knowledgable spectroscopist, on being asked the reason of this advance, would at once reply—The Bohr theory. The tendency, therefore, of every one is to view the present state of our knowledge as a post-Bohr development, and to discuss spectroscopic phenomena as part of a Bohr science. Whilst I would be the very last to deny the correctness of this attitude, since the achievement by Bohr in clarifying obscurity and placing all observations on a real scientific basis is a truly great one, yet I am inclined to regret the concomitant tendency to relegate all earlier theories to a sort of pre-glacial epoch, only worthy of consideration by historians who love to delve in the forgotten past. It may be felt that in these days of progress and scientific efficiency there is no time to concern ourselves with things that are dead and gone, but there I venture to join issue, for such an attitude kills romance, and I hold that there are few subjects of scientific nature which the Spirit of Romance has touched with her magic wand more deftly and more intriguingly than spectroscopy. What a fascinating story it makes. Not only do we delve into the secrets of Dame Nature as she reveals herself in this earth of ours, but also do we peer into the mysteries of the sun and stars, which guard secrets deeper still. Romance, after all, is the story of human achievement, whether it be of Theseus and the mysteries of the Labyrinth, of Stanley and the mysteries of Darkest Africa, or of Faraday and the mysteries of Science. Advance piled on advance into unknown fields of knowledge has a romance which is second to none if only we take thought of it. Who can in their hearts deny the romance that clings to the work of the great pioneers in our own field? What of Bunsen and Kirchhoff, of Huggins, of Rayleigh, and of Michelson? To me, too, there is an aura of romance in the work of Lockyer, who ranks among the pioneers in the advance into the uncharted domain where the sun and stars pursue their appointed course of evolution from the dim vastness of the inchoate nebula

[1] *Proc. Roy. Soc.*, **30**, 22 (1879). [2] *Ibid.*, **32**, 204 (1881).
[3] *Ibid.*, **60**, 475; **61**, 148 (1897); **65**, 452 (1899); "Tables of Wave-lengths of Enhanced Lines" (1906); "Researches on the Chemical Origin of Various Lines in Solar and Stellar Spectra" (1910), H.M. Stationery Office.

through the blazing giant star to the cold and dark mass only recognisable by its perturbing effect on the light and movement of its still brilliant companion. Those who bow the knee only to a mathematical formula and reverence its elegance do much to kill the spirit of romance and dim the glamour of our story. Let us all treasure the romance and glamour in our hearts lest we forget the deeds of derring-do of the past, lest we forget the noble foundations of knowledge laid by great men, on which it has been found possible to build so truly and so well.

As the result of his investigations Lockyer considered that the passage from the arc to the spark discharge meant a great increase of temperature, and that the enhanced lines were due to a very high temperature developed in the spark, although he included electric stress in the term "temperature." He distinguished between four different types of spectra as follows, iron being quoted as an example :—

1. The flame spectrum, consisting of relatively few lines only, including the well-known triplets and many strong lines in the ultra-violet.

2. The arc spectrum, consisting of some thousand lines.

3. The spark spectrum, differing from the arc spectrum in the enhancement of some of the short lines and the reduced brightness of others.

4. A spectrum consisting only of the lines which are intensified in the spark, and which would only be seen at the highest temperature.

Lockyer considered that the fourth type of spectrum was due to a new element formed by the decomposition or disintegration of the element which gives the lines of the spark spectrum. He was guided in formulating his ideas by his discovery of the enhanced lines of certain elements in the spectra of new stars or novæ, and he concluded that these stars and others, which also show these enhanced lines, are composed of the unknown elements which can only exist under the conditions of enormous temperatures. He indicated these unknown elements by prefixing the word proto to the name of the elements from which they are derived by means of the temperature or electric stress of the spark, the original view being that these elements form an earlier stage in the evolution of the known terrestrial elements.[1] He thus speaks of protocalcium, protomagnesium, protosilicon, etc., the spectra of which consist of the enhanced lines of the known elements.

After all, there is not so great a difference between Lockyer's views and those we now hold, since the loss of one or more electrons very naturally causes a marked change in the spectrum emitted. As we shall see in Vol. III., Chapter I., the phenomenon is of considerable interest, since, according to the law of Kossel and Sommerfeld, the

[1] I cannot here enter into the theories of stellar evolution, but would refer to a very interesting book which has recently been published, namely, *Astronomical Physics* (F. J. M. Stratton). Methuen, London, 1925.

spectrum of an atom which has lost one electron must be very analogous to the spectrum of the atom which precedes it in the periodic table of elements. Similarly, the loss of two electrons renders the resulting spectrum analogous to that of the element which is next but one in the descending order of atomic weights, and so on. This prediction has been completely verified, since the spectra of neutral sodium, singly ionised magnesium, doubly ionised aluminium, and trebly ionised silicon are all very similar to one another. Another remarkable instance is the very close similarity between the spectra of hydrogen and ionised helium, the latter, indeed, for some time being attributed to hydrogen. The difference between the spectra of the same atom in the neutral and ionised states is just the same as between two different elements, and consequently the assignment of the two spectra to two different elements, one being parent of the other, was, to say the least of it, justifiable. Indeed, in a process of evolution of an element the ionised atom might well be the penultimate stage in the sequence, stable only under the conditions prevailing in those stars which show the enhanced lines.

Quantitative Analysis by Spark Spectra.—In 1884 Hartley initiated a series of investigations which have been subsequently developed by Pollok, Leonard, and Whelan, and which have shown that it is possible to carry out quantitative estimations by means of spectroscopy. We may consider the work in some detail because of the interesting classifications of the spectrum lines which have resulted, as well as because it certainly has in many cases proved to be a valuable adjunct to the more classic methods of chemical analysis.

In his early work on the spark spectra of solutions of metallic salts Hartley showed that such spectra only show the lines of the metal and, further, that the effect of dilution of the solutions is to weaken these lines until they finally disappear. He also found that all the lines given by a metal in a solution of one of its salts do not disappear at the same dilution, some of the lines persisting over a much greater range of dilution than others. In addition to this, he proved that, provided the sparking conditions remain constant, the same lines always disappear at the same dilution. It is on this property that the quantitative estimation of the metals is based. The method, initiated, as I say, by Hartley, has been further investigated by Pollok, Leonard, and Whelan, with the result that it can be employed with more than ordinary confidence.[1]

We may first deal with the experimental technique, and here it is advisable always to conform, as far as possible, to the conditions laid down by Hartley and by Pollok. The best material to use for the electrodes is gold, and the following directions are given by

[1] The following papers contain a complete account of this work: Hartley, *Phil. Trans.*, **175**, 49, 325 (1884); *Proc. Roy. Soc.*, A, **69**, 283 (1902); J. H. Pollok, *ibid.*, **11**, 184 (1907); J. H. Pollok and A. G. G. Leonard, *ibid.*, **11**, 217, 229, 257 (1907); A. G. G. Leonard, *ibid.*, **11**, 269 (1908); J. H. Pollok, *ibid.*, **11**, 331 (1909); A. G. G. Leonard and P. Whelan, *ibid.*, **15**, 274 (1918).

Pollok for the sparking apparatus: A piece of glass capillary tube about 6 inches long is bent into the form of a U with limbs of unequal length, and a small cup like a miniature thistle funnel, of about 2 c.c. capacity, is blown at the end of each limb. The apparatus is shown in Fig. 48. A gold wire is passed through the capillary tube so as to project a little above the run of the lower cup, and a short length of thin-walled capillary glass tubing is slipped over the end of the gold wire and is made of such a length as just to reach the top of the wire. This outer tube draws up the solution and keeps the solution well wetted during the passage of the sparks. In order to guard against fusion it is necessary to use thick gold wire, and it is more economical to use only a short length of gold attached to a thin platinum wire which is sufficiently long to pass through a capillary tube.

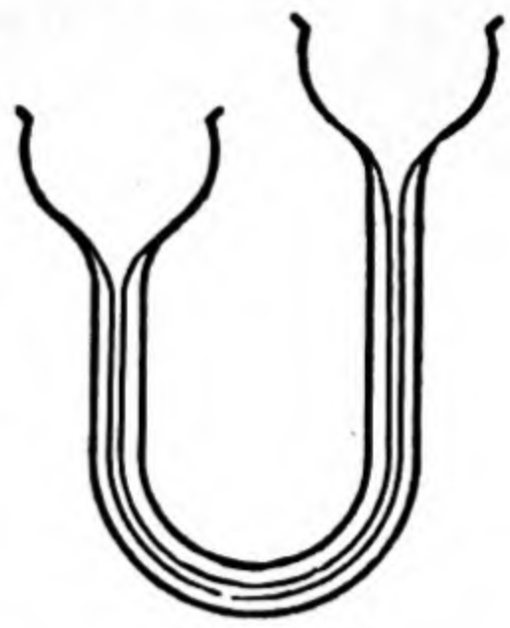


FIG. 48.

The upper gold electrode may be supported in any convenient manner, and must be attached to the positive pole of the induction coil, the solution being made negative. A condenser must be used in the circuit and, if it be desired to remove the air lines from the spectrum of the discharge, a self-induction coil may be used. In actual practice a photograph is taken of the spectrum given by the gold electrodes alone, using a long slit. The solution is then placed in the sparking apparatus, the slit shortened, and a second photograph taken. The lines characteristic of the substance under investigation will then be seen as short lines between the long lines of the gold electrodes, and their wave-lengths can be determined by interpolation between these, using Hartmann's formula.

Graphite or other materials may be used for the electrodes, but the result of experience is very decidedly in favour of the use of gold. Platinum suggests itself as a possibility, but its spectrum contains an inconveniently large number of lines. On the other hand, if in an investigation with gold electrodes, the presence of lines nearly coincident with gold lines is suspected, then platinum or graphite may be used.

The possible presence of impurities in the gold electrodes is obviously a matter of great importance. The most probable impurity is silver, and the only other metal likely to be present is copper. It is evident, therefore, that, unless these two metals have definitely been proved to be entirely absent from the gold wire used, it is impossible to test for these two particular metals with gold electrodes, and graphite or platinum must be used.

In his original work on the relative persistence of metallic lines as the concentration is decreased, Hartley used solutions of the chlorides wherever possible, and in cases where this is not possible, as, for example, in the case of silver, the nitrate may be used. His method was to photograph the spark spectra of solutions containing 1, 0·1,

0·01, and 0·001 per cent. of the metal ion respectively, and note the dilution at which the various lines disappeared. The relative persistence of the lines was indicated by Greek letters. This system of classification was extended by Pollok and Leonard, who employed the following symbols for the various persistencies of the lines :—

τ obtained with the metal, but not with strong solutions.

σ obtained with strong solutions, but not with 1 per cent. solutions.

ϕ obtained with 1 per cent. solutions, but not with 0·1 per cent. solutions.

χ obtained with 0·1 per cent. solutions, but not with 0·01 per cent. solutions.

ψ obtained with 0·01 per cent. solutions, but not with 0·001 per cent solutions.

ω obtained with 0·001 per cent. solutions.

One thing will at once be obvious to anyone who wishes to undertake work in this field, namely, that the question of the accurate determination of wave-length does not arise. All that is necessary is an accuracy of measurement, which is sufficient for the identification of the most persistent lines. Once these have been identified and the element to which they belong has been recognised, no difficulty whatever will be met with as regards the less persistent lines of that element when the quantity present is being estimated.

The difficulties met with by Hartley in his early work and also by Pollok have been largely removed, partly by the very great advance made in the design of spectrographic instruments. With a good spectrograph, such as that illustrated on pp. 118 and 119 of Vol. I., it is possible to obtain a spectrum photograph with the lines in perfect focus over the whole region involved in this work. With the help of a modern travelling micrometer the positions on a linear scale of the lines, those of the electrodes and of the elements under investigation, can be measured with accuracy. From a knowledge of the wave-lengths of the electrode lines, the wave-lengths of the unknown lines can be calculated by means of the Hartmann interpolation formula to an approximation fully sufficient to identify them. Moreover, one is also guided to a certain extent by a previous knowledge of the metals which are likely to be present.

The first matter, therefore, which concerns us is the wave-lengths of the lines given by the gold electrodes which may be used as standards in the spectrum photographs. It will be found that in general the more sensitive lines are found in the blue, violet, and ultra-violet regions, but in a few cases it is necessary to consider lines of longer wave-length. In Table XIII. are given the wave-lengths of the gold lines which may be used, and there are included the two D lines of sodium, as these generally are present, and the strongest air lines which may appear with small self-induction coils in the circuit. In this table, and in all subsequent tables, the wave-lengths are expressed on the international standard. In the original papers the wave-lengths given were somewhat out of date, and I have thought it

advisable to bring them as far as possible into line with present-day work.

TABLE XIII.

STANDARD ELECTRODE LINES.

No. of lines.	λ.	Element and intensity.	No. of lines.	λ.	Element and intensity.
2	6456·52	Au 5	22	2675·95	Au 12
3	6278·29	Au 4	23	2641·52	Au 6
—	5895·93	Na 10	24	2590·09	Au 6
—	5889·96	Na 10	25	2544·21	Au 5
4	5837·42	Au 6	26	2503·29	Au 8
5	5679·5	N 12	27	2473·83	Ag 8
6	5465·49	Ag 10	28	2447·79	Ag 8
7	5230·31	Au 8	29	2437·67	Ag 10
8	5005·2	N 10	30	2427·97	Au 10
	5001·4	N 10			
9	4792·61	Au 8	31	2413·08	Ag 10
10	4488·26	Au 8	32	2387·76	Au 4
11	4315·15	Au 8	33	2364·7	Au 10
12	4065·08	Au 15	34	2352·6	Au 6
13	3897·89	Au 10	35	2331·25	Ag 8
14	3586·5	Au 7	36	2304·81	Au 8
15	3582·87	Ag 10	37	2283·34	Au 5
16	3280·66	Ag 10	38	2242·7	Au 5
17	3122·80	Au 10	39	2229·0	Au 6
18	3029·20	Au 6	40	2201·3	Au 5
19	2913·52	Au 9	41	2188·9	Au 5
20	2825·45	Au 9	42	2166·5	Ag 4
21	2748·25	Au 5			

Pollok numbered the lines for purposes of reference, commencing with the lithium line $\lambda = 6707{\cdot}87$, which was used if required. The wave-lengths which are given only to the first place of decimals in Table XIII. are less accurate than the others. It will be found that in the majority of cases there is no need to carry the classification of spectrum lines outside the limits of the lines Nos. 9 and 25.

As will be obvious from what has already been said, the whole method is based on the persistence of the lines, and it was Hartley who was the first to point out that the most persistent lines are not necessarily the most intense. The method of classification of the lines of a spectrum has already been given, in which the Greek letters ϕ, χ, ψ, ω are given to lines in ascending order of their persistence. Some elements, of course, do not exhibit any ω lines, and some do not even exhibit any ψ lines. As Pollok remarks, in order to determine whether an element is present or not, it is only necessary to look for the most persistent lines, and if these are absent then that element is not present, whatever apparent coincidences may occur as regards the other lines of that element. The most persistent lines of an element are called by Pollok the residuary lines of that element, and are

denoted by ϕ, χ, or ω, according to the dilution at which they disappear.

Before giving instances of how the persistence of lines has been applied to quantitative analysis, the tables may be given of the relative persistence of the lines of the metallic elements. As in the case of the electrode lines, I give the wave-lengths of the lines in I.A., and have amended the lists given by Hartley, Pollok, and Leonard to a certain extent. In the first place, a few lines which are not included in the most recent wave-length tables have been deleted because these must have been due to traces of impurities in the metals investigated. I have thought it preferable, too, to quote as the intensities those values given by the most recent observers of the spectra of the pure elements.

In general, the persistence of the lines was determined by sparking solutions of the chlorides. The lines of silicon are not given on sparking acid solutions, and large quantities of this element may be present in acid solutions of metallic salts without any indication being given of its presence. The silicon lines were observed by sparking a solution of sodium silicate. For the molybdenum lines a solution of ammonium molybdate was used, and in the case of tungsten a solution of sodium tungstate. Thorium nitrate in solution was employed for the lines of this metal.

There is one precaution which it is very necessary to take in certain cases. It is very possible in sparking strong solutions to dissipate particles of the salt under investigation into the atmosphere, with the result that correct values are not obtained for the persistence when more dilute solutions are subsequently sparked, the values erring on the side of too great a persistence. As pointed out by Pollok, some of Hartley's earlier observations are for this reason subject to correction. In order to guard against this source of error it is advisable always to commence with the most dilute solutions and then to follow with solutions of increasing concentrations.

TABLE XIV.

First Group of Elements.

Lithium.

6707·87	20ω
6103·59	10ψ
4602·19	8ω
4132·3	5ψ
3232·67	6φ

Sodium.

5895·93	20ω
5889·96	20ω
5688·04	6ψ
5682·68	6ψ
3302·96	10χ
3302·35	15χ
2852·80	10σ

Potassium.

4047·21	10φ
4044·15	10φ
3447·38	8σ
3446·38	10σ

Rubidium.

4571·67	5χ
4293·92	10σ
4273·10	3τ
4244·34	15σ
4215·56	10σ
4201·82	15σ
4104·34	8σ
3940·47	15σ
3601·20	3σ
3522·1	2σ
2472·26 ?	2τ

Cæsium.

4593·18	3ω
4555·36	4ω
4538·94	6ω
3959·50	5σ
3925·58	6σ
3661·39	6σ
3268·31	2φ

Cæsium—(contd.).

2859·39	2σ
2630·57	3χ
2600·36	1σ
2596·93	2φ
2525·75	1ω
2485·50	1φ
2455·89	1φ
2392·92	2φ

Copper.

3307·96	8χ
3290·48	10φ
3273·94	10ψ
3247·53	10ω
2961·13	4φ
2713·67	8χ
2701·15	9φ
2689·46	4χ
2600·42	7φ
2544·96	10χ
2529·46	8χ
2506·42	10χ
2492·13	4φ
2489·62	6φ
2473·47	2φ
2369·88	10χ
2294·37	5φ
2247·01	8χ
2242·61	6χ

Silver.

3382·92	40ψ
3280·66	30ψ
2938·49	5φ
2767·52	20χ
2711·9	20χ
2660·36	15χ
2580·70	15φ
2506·37	9χ
2477·26	10φ
2473·83	10χ
2453·29	10φ
2447·79	12χ
2437·67	15ψ
2429·62	12χ
2420·07	8χ
2413·08	15ω

Silver—(contd.).

2411·78, 2411·36	10χ
2375·05	10φ
2358·85	6χ
2357·76	8χ
2331·25	9ψ
2324·56	7ψ
2320·14	9ψ
2316·92	8ψ
2279·88	6χ
2248·58	4χ
2246·30	5ψ

Gold.

4792·61	8χ
4488·26	5σ
4065·08	10σ
4016·05	5σ
3927·57	4χ
3586·5	5φ
3133·02	2χ
3122·80	8χ
3033·2	2φ
2995·00	5σ
2990·28	5σ
2954·43	4σ
2918·40	2χ
2913·52	10σ
2838·03	2φ
2825·45	4σ
2819·97	8σ
2805·31	2σ
2802·20	20σ
2780·84	3σ
2748·26	8φ
2688·70	3φ
2688·15	3φ
2687·62	3φ
2675·95	20χ
2641·49	4χ
2503·30	5φ
2352·66	3φ
2304·80	3φ
2283·30	3φ
2263·75	2σ
2219·21	1σ
2215·15	1σ
2201·33	2χ

TABLE XV.

SECOND GROUP OF ELEMENTS.

Magnesium.

5528·42	4φ
5183·60	20φ
5167·32	10φ
4703·00	5τ
4481·17	20σ
4351·91	8τ
3838·29	10σ
3832·30	10σ
3829·35	8σ
3336·69	8σ
3332·16	5σ
3329·93	6σ
3096·91	10φ
3093·01	8φ
2936·76	20χ
2928·64	20χ
2915·47	10σ
2852·13	20ω
2798·00	20ω
2790·80	20ω
2782·95	6φ
2781·42	5φ
2779·84	10χ
2778·28	5φ
2776·70	6φ

Calcium.

5594·45	7σ
5270·27	8σ
4878·16	7σ
4585·90	6σ
4581·44	5σ
4527·00	4σ
4454·78	10φ
4434·96	9φ
4425·45	10φ
4318·64	7σ ?
4307·74	6σ
4302·53	9σ
4298·98	6σ
4289·36	5φ
4283·00	7φ
4226·72	10ω
3968·48	40ω
3933·67	50ω
3736·91	10ψ
3706·03	10ψ
3644·35	4φ
3630·70	4φ
3179·32	10χ
3158·88	10χ

Strontium.

5534·80	7σ
5521·80	7σ
5504·26	8σ
5486·15	4φ
5480·94	10φ
5450·86	5σ
5256·95	6σ
4962·27	15φ
4876·07	4σ
4832·07	6σ
4811·83	8σ
4741·89	4σ
4722·27	4σ
4607·34	20ω
4305·49	20ω
4215·52	30ω
4161·83	20φ
4077·75	50ω
4032·35	1σ
3474·90	6φ
3464·4	20φ
3380·8	15σ
3351·3	15χ

Barium.

5535·53	10φ
5519·12	8φ
5424·61	5σ
4934·10	10ψ
4899·97	8σ
4726·46	5σ
4691·63	5σ
4673·62	7σ
4554·04	10ω
4524·95	7χ
4505·94	6σ
4431·91	6σ
4402·55	6σ
4350·38	5σ
4283·11	8σ
4166·02	7φ
4130·68	8ω
3993·40	7σ
3909·92	6σ
3891·79	8ψ
3501·11	5σ
3356·89	6σ
2771·36	3φ
2634·80	7φ

Zinc.

4810·53	20φ
4722·16	20φ
4680·14	20φ
3345·51	8 }
3344·99	12 } χ
3302·91	10 }
3302·56	12 } χ
3282·28	10χ
3075·88	5σ
3072·07	8σ
3035·81	5σ
3018·38	4σ
2800·9	8φ
2770·84	6φ
2756·45	4φ
2712·50	4σ
2684·20	5σ
2582·51	6σ
2569·91	4σ
2558·01	12χ

Cadmium.

3612·89	6ψ
3610·51	10ψ
3467·63	4ψ
3466·20	6ψ
3403·60	6χ
3261·05	6φ
2748·6	10χ
2321·16	8φ
2312·82	10ψ
2288·03	10ψ
2265·03	8ω
2194·63	4φ
2144·39	4φ

Mercury.

3663·27	10φ
3654·83	10φ
3131·85 }	10χ
3131·56 }	
3125·62	8φ
2967·28	10χ
2847·67	8φ
[1] 2534·80	6ω
2224·67	5φ

[1] There seems to be an error here; the line having the greatest persistence should be the one with wave-length $\lambda = 2536{\cdot}52$.

TABLE XVI.

THIRD GROUP OF ELEMENTS.

Aluminium.

3961·54	10ω
3944·03	10ω
3586·81	20φ
3092·83	6 } ψ
3092·71	10 } ψ
3082·15	10ψ
2816·30	10χ
2660·39	10φ
2652·46	10φ
2575·41	4 } φ
2575·11	10 } φ
2567·99	10φ

Indium.

4511·37	10χ
4101·82	12χ
3258·55	6φ
3256·03	8ψ
3039·36	4ψ
2941·21	6χ
2932·62	5φ
2710·31	10χ
2560·22	6φ
2306·14	4χ

Thallium.

3775·73	10ψ
3519·23	10χ
2918·32	12φ
2767·87	10ψ
2298·18	6χ

Yttrium.

5648·46	4φ
5581·88	8φ
5544·60	4φ
5497·43	8φ
5466·47	10φ
5402·79	4φ
5205·73	10φ
5087·42	10χ
4900·13	20χ
4883·71	20χ
4854·89	15φ
4674·85	5φ
4643·68	5φ
4527·80	8 } φ
4527·25	9 } φ
4422·60	10φ
4374·94	20ψ
4309·63	12φ
4177·53	20ψ
4142·86	8φ
4128·32	8φ
4102·40	8φ
3982·60	12φ
3832·90	10φ
3788·69	20φ
3774·34	30χ
3710·29	15χ
3664·51	12φ
3611·15	15χ
3600·74	20χ
3549·00	12φ
3496·08	8φ
3327·88	15φ
3242·28	15ψ
3216·69	12χ
3200·26	8φ
3195·61	8φ
3173·05	8φ
2946·04	12χ
2816·99	15χ
2460·68	4φ
2422·21	6χ
2414·70	10χ

Lanthanum.

5588·33	6χ
5455·14	8χ
5377·10	5φ
4920·95	8χ
4899·91	5χ
4743·08	10φ
4692·50	5φ
4663·77	6φ
4655·50	8φ
4522·37	10χ
4429·90	10φ
4333·77	12φ
4296·05	8φ
4286·97	12φ
4269·50	10φ
4263·59	8φ
4238·40	10φ
4196·55	10φ
4123·24	15φ
4077·34	12φ
4031·70	15φ
3988·52	15χ
3949·10	20ψ
3790·82	20φ
3759·07	12φ
3517·11	20φ
3344·55	7φ
3337·49	12φ
3171·66	20ψ
2808·36	4χ
2695·49	1φ
2685·0	1φ
2651·68	8φ
2610·34	5χ
2596·11	1φ
2560·41	1φ
2519·22	2φ
2487·56	1φ
2476·71	7χ
2399·65	1φ
2379·41	10ψ
2297·83	7χ

TABLE XVII.

FOURTH GROUP OF ELEMENTS.

Silicon.

4130·9	6φ
4127·9	5φ
3905·5	4φ
2881·59	15φ
2631·29	6φ
2528·52	8ψ
2524·12	7φ
2519·21	6φ
2516·12	10ψ
2514·33	6φ
2506·90	6φ

Tin.

3801·03	10χ
3352·33	10χ
3330 61	5χ
3262·31	30χ
3175·04	20χ
3032·79	6χ
3009·14	10χ
2913·54	6φ
2896·12	3φ
2863·32	15ψ
2850·62	6φ
2813·58	4χ

TABLE XVII.—*Continued.*

Tin—(contd.).

2779·81	4χ
2706·51	10ψ
2658·61	10χ
2643·60	6χ
2631·87	4χ
2594·41	4φ
2571·58	5χ
2546·54	4χ
2495·71	4φ
2483·41	4χ
2429·50	10ψ
2421·71	10χ
2354·86	4χ
2334·80	5φ
2317·24	6φ
2246·06	6φ

Lead.

3740·00	12χ
3683·47	6χ
3639·57	12χ
3572·77	12ψ

Titanium.

5210·39	8φ
5064·66	7φ
5014·26	7φ
5007·22	8φ
4999·51	9φ
4991·08	10φ
4981·75	11χ
4805·43	4 } φ
4805·11	7 } φ
4759·28	8φ
4758·13	8φ
4571·98	15φ
4563·77	8φ
4549·64	15φ
4533·97	9χ
4468·49	12χ
4395·04	12χ
4300·05	9χ
3958·21	8χ
3948·66	8χ
3761·33	12ω
3759·30	15ω
3752·87	5φ
3741·14	8χ
3685·19	15ω
3653·49	8φ
3642·68	9φ

Titanium—(contd.).

3510·84	15χ
3504·89	15χ
3477·18	9φ
3461·51	9φ
3444·33	8χ
3394·57	10χ
3387·83	8φ
3372·80	10ω
3361·22	10ω
3349 41	8 } ω
3349·02	7 } ω
3341·87	9ψ
3340·33	8ψ
3335·19	10φ
3329·45	10φ
3326·76	8φ
3322·93	10ψ
3321·70	4ψ
3287·64	10φ
3261·59	18ψ
3252·85	10ψ
3248·60	9φ
3241·97	12χ
3239·65	7 } χ
3239·03	8 } χ
3236·57	10χ
3234·52	12χ
3229·18	7ψ
3224·23	7φ
3222·82	8φ
3218·25	8ψ
3202·52	6χ
3190·87	7ψ
3168·52	8χ
3162·56	8ψ
3088·03	8ψ
3078·64	8χ
3072·10	7χ
3066·36	5χ
3058·08	7χ
3017·18	10φ
2941·99	9φ
2884·10	8φ
2877·42	8χ
2862·21	8χ
2841·91	10χ
2828·15	7χ
2817·84	8φ
2810·28	8χ
2751·70	8φ
2746·70	6φ
2742·30	4φ
2739·80	1φ
2646·08	5χ
2644·22	3φ
2571·07	4φ
2567·53	7χ

Titanium—(contd.).

2565·42	8φ
2563·42	10φ
2540·02	10χ
2535·90	5φ ?
2534·63	6φ
2531·30	8χ
2527·84	15φ
2525·62	10χ

Zirconium.

4772·31	6φ
4738·48	9φ
4710·08	9φ
4687·81	10φ
4574·48	4φ
4535·75	7φ
4496·96	9φ
4442·99	10φ
4379·77	12φ
4370·95	9φ
4359·74	10φ
4208·96	10φ
4161·21	9φ
4149·20	20φ
4029·67	5φ
4024·91	5φ
3998·96	15φ
3991·13	12φ
3958·22	15χ
3836·83	20χ
3766·81	10φ
3751·59	20φ
3746·03	15φ
3731·25	15φ
3709·26	15φ
3698·16	20χ
3678·88	6χ
3674·70	15χ
3601·18	7ψ
3578·21	3φ
3578·85	15φ
3572·47	12ψ
3556·59	15φ
3542·62	15φ
3505·66	10 } χ
3505·48	10 } χ
3497·90	8χ
3496·20	20χ
3481·15	15χ
3463·01	15φ
3440·43	2χ
3438·23	20φ
3430·52	10φ
3419·11	3ψ
3410·25	8ψ

TABLE XVII.—*Continued.*

Zirconium—(contd.).		*Cerium.*		*Thorium.*	
3394·64	2ω	5512·08	7χ	4391·12	10ψ
3391·98	20ω	5472·28	6φ	4381·89	10ψ
3388·30	5 ψ	5353·53	6φ	4116·75	6χ
3387·88	5 ψ	5274·23	5φ	4019·14	10χ
3356·09	4φ	5187·43	6φ	3741·23	6χ
3340·55	6φ	5079·69	4χ	3711·35	3χ
3334·24	4χ	4714·00	3φ	3538·75	10χ
3306·27	8φ	4628·15	10φ	3469·94	5χ
3284·71	4φ	4606·41	5φ	3402·68	4χ
3279·27	8φ	4593·93	10φ	3354·61	2 σ
3273 04	10χ	4572·27	10φ	3354·22	3 σ
3241·05	4φ	4560·27	5φ	3351·25	4σ
3234·12	2φ	4539·73	8φ	3334·59	4σ
3214·19	4χ	4528·37	8 χ	3325·14	4σ
3182·87	5χ	4527·34	8 χ	3300·6	12χ
3165·98	4ψ	4471·23	6φ	3290·59	10ψ
3138·68	4ψ	4460·21	10φ	3188·22	5χ
3133·48	4φ	4444·70	4 φ	3141·82	2σ
3129·75	4φ	4444·40	3 φ	3139·26	4σ
3106·57	4χ	4428·44	4 φ	3108·27	5χ
3054·82	4ψ	4427·92	4 φ	3078·84	6χ
3036·48	3ψ	4418·78	5φ	3034·08	3χ
3024·44	2χ	4410·76	2 φ	3008·48	2χ
3003·72	2χ	4410·65	2 φ	2978·68	8χ
2926·97	4ψ	4391·67	8φ	2942·90	3φ
2869·79	3χ	4382·17	5φ	2925·05	2φ
2844·56	4ψ	4364·66	5φ	2898·92	6χ
2818·72	3φ	4352·71	3φ	2895·15	2φ
2810·90	3φ	4266·76	8φ	2870·43	3ψ
2774·15	3φ	4285·38	3φ	2861·38	3χ
2768·70	3φ	4270·72	3 φ	2842·81	2φ
2758·79	3φ	4270·19	3 φ	2832·35	4χ
2752 18	3φ	4181·08	3χ	2771·51	3χ
2745·83	3φ	4165·60	10χ	2768·85	4χ
2742·53	4φ	3940·97	3	2764·65	2χ
2734·83	5φ	3940·67	1 χ	2760·41	2χ
2732·69	3φ	3940·34	3	2752·20	3χ
2726·46	5φ	3730·34	1 φ	2747·17	3χ
2722·58	5φ	3729·92	1 φ	2729·30	3χ
2720·04	2φ	3719·79	1φ	2722·37	2χ
2715·75	3φ	3709·58	3 φ	2716·27	2χ
2714·23	3φ	3709·29	3 φ	2708·20	4χ
2711·48	3φ	3243·37	1φ	2703·95	3χ
2709·03	3φ	3234·89	1 φ	2695·20	2φ
2700·10	4φ	3234·16	1 φ	2692·40	3φ
2690·53	4φ	3218·95	1 φ	2686·17	6φ
2686·32	4φ	3218·38	1 φ	2684·33	3φ
2682·21	5φ	3201·71	2 φ	2625·73	2χ
2678·60	5φ	3201·10	2 φ	2618·92	2χ
2664·30	5χ	3194·82	3 φ	2600·91	2χ
2656·48	3χ	3194·10	3 φ	2597·06	2χ
2643·80	5φ	3169·18	1φ	2583·39	4χ
2630·87	3ψ	3143·93	2φ	2571·63	5χ
2628·25	3χ	3056·54	2χ	2564·41	6φ
2620·57	8χ	3055·59	4χ	2555·22	4ψ
2571·39	8ψ	2651·01	1φ	2554·71	4ψ
2568·84	6ψ	2635·15	1φ	2549·57	4 ψ
2550·77	3φ	2603·63	3χ	2549·12	3 ψ
2542·09	3χ	2578·31	1φ		
2532·45	3φ	2548·79	1φ		

TABLE XVIII.

Fifth Group of Elements.

Arsenic.

2860·46	8φ
2780·23	10χ
2349·84	5φ

Antimony.

3739·95	4φ
3597·51	1φ
3504·51	5φ
3337·15	1φ
3267·53	4φ
3232·54	3φ
3029·86	4χ
2877·92	4ψ
2790·39	5χ
2598·08	6ψ
2528·54	12χ
2311·48	6φ

Bismuth.

3792·85	15φ
3695·55	15φ
3596·15	8φ
3510·85	8φ
3397·21	10φ
3067·69	10ψ
3024·63	10χ
2993·31	8φ
2938·30	15φ
2897·99	10χ

Vanadium.

4462·38	10ψ
4460·29	10ψ
4408·50	20ψ
4400·57	10φ
4395·24	15φ
4389·98	20φ

Vanadium—(contd.).

4384·73	30φ
4379·24	30ψ
4131·98	10φ
4128·10	10φ
4115·17	6φ
4111·80	20φ
4023·35	20φ
4005·73	20φ
3863·88	4φ
3855·84	3φ
3840·75	2φ
3750·88	4φ
3745·81	20φ
3732·76	20φ
3727·46	20φ
3715·47	20φ
3709·36	3χ
3593·33	15φ
3545·19	30χ
3517·29	20χ
3457·16	10φ
3276·13	20χ
3271·13	20χ
3267·62	20χ
3217·12	10φ
3190·67	10φ
3187·70	8φ
3185·40	4χ
3183·98	2 } χ
3183·41	2 } χ
3142·49	3φ
3139·78	8φ
3136·53	8φ
3134·94	8φ
3133·34	5φ
3130·28	10φ
3118·38	15ψ
3110·70	15ψ
3102·29	15ψ
3093·12	15ψ
3067·12	5φ
3063·26	4φ
3057·06	1φ

Vanadium—(contd.).

3008·61	5φ
3003·47	4φ
3001 18	8χ
2976·49	3φ
2968·37	10φ
2957·50	6φ
2952·07	8φ
2944·56	8χ
2941·42	10χ
2924·62	8ψ
2920·42	3φ
2910·44	4φ
2909·96	4φ
2908·81	7φ
2903·11	4φ
2896·25	4φ
2891·66	6φ
2889·64	4φ
2888·26	4φ
2880·07	5φ
2877·69	2φ
2869·14	5φ
2854·35	5φ
2810·26	8φ
2777·72	3φ
2775·76	3φ
2753·40	5χ
2742·43	2φ
2739·71	3φ
2728·64	5χ
2715·67	5χ
2714·17	2φ
2706·75	2 } χ
2706·13	3 } χ
2702·20	3χ
2690·83	2φ
2683·12	2χ
2679·31	4φ
2672·00	3χ
2663·30	6χ
2655·70	6φ
2649·43	5φ
2630·66	3φ

TABLE XIX.

Sixth Group of Elements.

Chromium.

4289·73	10ψ
4274·80	10ψ
4254·34	10ψ
3605·33	10χ
3593·48	10χ
3578·69	10χ

Chromium—(contd.).

3422·74	20φ
3421·21	10φ
3408·77	20φ
3403·32	15φ
3180·70	10φ
3132·05	20φ

Chromium—(contd.).

3030·25	5φ
3029·17	4φ
3024·36	5φ
3021·57	6φ
3020·67	5φ
3018·83	4φ

TABLE XIX.—*Continued.*

Chromium—(contd.).

3018·50	5φ
3017·58	6φ
3015·20	4φ
3014·92	6φ
3014·77	6φ
3013·72	4φ
3013·04	4φ
2988·65	5φ
2980·80	4φ
2971·91	8 } φ
2971·12	4 } φ
2953·71	4 } φ
2953·37	3 } φ
2843·25	10ψ
2835·64	10ψ
2830·47	10ψ
2766·54	8φ
2762·60	8φ
2698·85	4 } φ
2698·70	4 } φ
2698·42	4 } φ
2663·68	3 } φ
2663·43	5 } φ
2658·60	4φ
2653·59	5φ

Molybdenum.

5570·46	12σ
5533·01	12σ
5506·51	15σ
4760·21	5φ
4731·45	5φ
4707·25	6φ
4381·66	6χ
4244·78	6φ
3902·95	10ψ
3864·11	10ψ
3798·25	10ψ
3688·32	12χ
3614·27	5σ
3524·61	3χ
3402·82	8χ
3254·70	3χ
3253·81	4χ
3244·49	2σ
3240·73	4χ
3237·83	2χ
3222·92	2σ
3208·86	4σ
3200·27	3χ
3195·93	3χ
3192·12	3χ
3176·31	5χ
3175·06	5χ
3172·77	4χ

Molybdenum—(contd.).

3159·27	2σ
3155·63	4σ
3145·73	2σ
3141·77	3σ
3141·37	3σ
3138·76	3σ
3132·64	2φ
3132·53	2φ
3110·85	3φ
3092·11	5φ
3087·60	10φ
3077·64	8φ
2963·81	4φ
2923·39	10ψ
2911·90	10φ
2903·07	10φ
2894·44	5χ
2888·15	4χ
2879·03	8φ
2871·49	10ψ
2866·67	5σ
2863·77	8ψ
2853·15	10χ
2848·19	12ψ
2816·13	15ψ
2807·72	6φ
2785·00	8ψ
2780·03	10σ
2775·40	12ω
2746·30	5φ
2717·31	8φ
2684·12	10ψ
2681·37	6ψ
2673·30	5ψ
2660·58	10ψ
2653·33	7φ
2646·46	8χ
2644·31	12χ
2638·74	10χ
2602·82	5φ
2600·16	5φ
2595·38	4φ

Tungsten.

4680·51	6φ
4659·84	5φ
4609·92	4σ
4302·12	6φ
4294·62	10χ
4269·39	5φ
4074·36	6χ
4069·91	5χ
4008·77	10χ
3780·77	4φ
3768·45	4φ

Tungsten—(contd.).

3750·79	2φ
3617·53	5φ
3215·57	5χ
3051·29	6χ
3049·86	3 } χ
3049·68	1 } χ
3024·49	5φ
3017·43	2φ
2979·88	3φ
2977·14	2φ
2946·99	3χ
2944·38	3χ
2934·99	3φ
2923·09	1σ
2896·04	2φ
2879·40	2ψ
2866·34	2φ
2848·01	1φ
2831·41	2ψ
2774·50	3φ
2764·30	6χ
2729·59	4φ
2724·09	4χ
2709·59	4φ
2702·11	10φ
2697·60	6χ
2694·71	2 } φ
2694·50	2 } φ
2697·62	6χ
2664·32	6φ
2658·03	7χ
2656·50	3χ
2653·56	2χ
2647·72	5χ
2632·73	2φ
2620·23	5φ
2615·33	4χ
2608·37	1χ
2603·04	5χ
2581·19	4φ
2572·31	6ψ
2563·15	5ψ
2555·15	3 } φ
2554·90	2 } φ
2551·42	3φ
2530·98	3χ
2522·03	2σ

Uranium.

4605·19	4φ
4603·68	4φ
4543·63	8φ
4415·26	3φ
4371·79	3φ
4355·65	4φ

TABLE XIX.—*Continued.*

Uranium—(contd.).		*Uranium*—(contd.).		*Uranium*—(contd.).	
4341·71	4φ	3672·60	2ψ	3057·93	2χ
4241·68	4ψ	3552·19	2ψ	3044·13	2χ
4171·59	4φ	3453·56	2φ	2971·06	2φ
4090·13	4χ	3436·80	2φ	2941·87	2χ
3954·65	2χ	3337·77	2χ	2887·20	1φ
3874·03	2φ	3270·16	2φ	2865·63	2χ
3859·55	3φ	3244·20	2φ	2793·95	2φ
3782·84	2φ	3093·04	2χ	2635·49	2χ
3693·73	2χ	3072·79	2φ	2549·32	2φ

TABLE XX.

Seventh Group of Elements.

Manganese.		*Manganese*—(contd.).		*Manganese*—(contd.).	
4823·52	8σ	3806·86	8φ	2879·48	5φ
4783·45	6σ	3495·85	8φ	2705·71	8φ
4083·62	6σ	3488·68	10φ	2701·69	4φ
4055·55	6σ	3482·92	10φ	2639·81	5φ
4048·73	6σ	3474·14	8 } φ	2632·37	7φ
4041·34	8σ	3474·06	8 }	2625·60	7φ
4035·72	5σ	3460·33	10φ	2618·11	8φ
4034·48	8σ	3442·00	10φ	2605·69	10ω
4033·06	8σ	2942·22	9χ	2593·71	12ω
4030·80	8χ	2939·31	8χ	2576·15	15ω
3823·51	5φ	2933·07	8χ		

TABLE XXI.

Eighth Group of Elements.

Iron.		*Iron*—(contd.).		*Iron*—(contd.).	
4415·13	10σ	3610·16	3φ	2684·76	4φ
4404·75	15σ	3608·86	6φ	2666·64	4φ
4383·55	20φ	3581·20	10χ	2664·67	4φ
4325·77	15σ	3570·10	10χ	2631·33	3ψ
4307·91	15σ	3565·38	5χ	2628·30	8ψ
4271·77	10σ	3490·58	4φ	2625·68	4 } ψ
4260·48	10σ	3475·46	3χ	2625·50	3 }
4250·79	6σ	3465·87	3χ	2621·67	4χ
4071·75	8σ	3440·99	4χ	2617·62	6χ
4045·82	15σ	3021·08	3ψ	2613·83	8χ
4005·25	6σ	3020·64	3ψ	2611·88	10χ
3859·91	6σ	2973·24	2χ	2607·10	10χ
3827·83	8σ	2970·11	2χ	2599·40	20ψ
3815·84	10σ	2966·90	3χ	2598·37	8ψ
3767·19	5φ	2965·26	2χ	2585·88	10χ
3749·47	10φ	2783·70	5φ	2566·92	3χ
3745·55	5φ	2767·52	5ψ	2562·54	5ψ
3737·13	6ψ	2755·74	15ψ	2549·61	4χ
3734·87	10ψ	2746·49	10φ	2533·80	3χ
3722·57	4ψ	2743·20	8χ	2529·83	3φ
3719·94	10ψ	2739·55	15ψ	2526·26	3φ
3687·46	4φ	2727·54	5χ	2525·40	4φ
3647·85	6φ	2714·42	5χ	2522·86	3χ
3631·46	6φ	2692·66	4φ	2511·77	5χ
3618·77	6φ				

TABLE XXI.—*Continued.*

Cobalt.		*Cobalt*—(contd.).		*Nickel*—(contd.).	
4530·95	10σ	2694·68	8ω	3472·53	5φ
4469·56	5σ	2663·53	15χ	3446·27	9χ
4121·33	10φ	2587·23	10φ	3433·58	6χ
4118·78	10σ	2582·25	15χ	3423·71	5φ
3995·31	10φ	2580·33	20ψ	3414·82	10ψ
3894·09	15ψ	2564·04	15φ	3392·97	7φ
3873·07	12ψ	2559·41	10χ	3232·93	10φ
3845·45	15φ	2528 62	5χ	3134·10	10χ
3502·30	6χ	2519·82	10ω	3101·88	8χ
3489·40	7φ			3101·56	6χ
3474·00	8χ			3064·63	6φ
3465·80	5φ	*Nickel.*		3057·63	8ψ
3453·50	10ψ			3054·31	6ψ
3449·44	5φ	3619·39	15φ	3050·82	10ψ
3443·65	6φ	3597·70	6φ	3037·93	8χ
3433·04	6φ	3566·37	10φ	3012·02	8χ
3412·64	10φ	3524·53	15χ	3003·65	6χ
3405·11	10ψ	3516·09	10χ	2545·92	6φ
3086·78	5φ	3510·33	10χ	2510·94	10ψ
3072·34	5φ	3492·96	10χ		

Two instances where this method was applied to quantitative analysis may be quoted. In one case Hartley was able to determine the composition of a coin which he found to contain

Lead	13·96 per cent.
Copper	72·35 ,,
Zinc	12·70 ,,
Iron	0·85 ,,

He subsequently proved these figures to be correct by comparison of the spectrum with those of similar alloys of known composition. In this particular case the method had the great advantage of obviating the dissolution of any part of the coin, which was a very ancient one, in acid.

In another case a dolomitic limestone was analysed for magnesium and calcium by conversion into the chlorides and examination of the spark spectra at different dilutions. Hartley concluded that the mineral contained

Magnesium	1 per cent.
Calcium	37 ,,

but he considered that it was possible that the calcium value was a little too high. Two independent analyses by ordinary chemical methods gave

Magnesium . .	1·17 per cent. and	1·38 per cent.
Calcium . . .	36·45 ,, ,,	36·98 ,,

Very similar investigations were carried out by the late Comte de Gramont, and his results in the main confirm those obtained by Pollok

and by Leonard. De Gramont's observations were, perhaps, more rigidly carried out, and there is no doubt that as the result of his very extended series of measurements considerable confidence may be felt as to their accuracy.

De Gramont did not deal to any great extent with the spark spectra of aqueous solutions of metallic salts, but he examined the spectra given by metallic alloys of known composition, and also by fused sodium carbonate containing known amounts of certain metallic oxides in solution. He also invoked the aid of the oxy-hydrogen and oxy-acetylene flame as a means of exciting the spectra. He selected by his work the most sensitive lines in each spectrum, that is to say, those lines which persist as the concentration is reduced. He denotes these as " raies de grande sensibilité," or " raies sensibles." Some of these lines alone persist to the greatest dilutions, and these he calls " raies ultimes." These are the spectrum lines which Pollok called the residual lines, but in using this name care must be taken to avoid confusion with the residual rays of Rubens, which are the long wave infra-red rays for which the reflecting power of a polished surface is a maximum.

Very many papers on this work were published by de Gramont,[1] and in these papers he frequently uses the term " dissociation spectra " in describing these observations.

De Gramont was led to undertake these investigations by his work on the spark and flame spectra of minerals, which, as can readily be understood from what has previously been said, revealed the fact that when an element is present in small quantities relatively few of its characteristic lines make their appearance. The condensed spark discharge was employed with and without a self-induction coil in the circuit. The results obtained were very similar to those previously recorded, for de Gramont found :—

1. That the sensitive lines are unaffected by the use of the self-induction coil.

2. That these lines appear both in the arc and spark spectra of the element, and that they are generally very intense in the former and not necessarily so in the latter.

3. That they are also present in the flame spectra as given by the oxy-hydrogen or oxy-acetylene flame.

The persistence of these lines was examined over great ranges of concentration, but the values obtained need not be given in view of their general resemblance to those already recorded. Moreover, in the application of this method to quantitative analysis it is advisable

[1] A. de Gramont, *Comptes Rendus*, **144**, 1101 (1907); **145**, 231, 1170 (1907); **146**, 1260, 1438 (1908); **147**, 239, 307 (1908); **149**, 263, 580 (1909); **150**, 37, 154 (1910); **151**, 308 (1910); **153**, 318 (1911); **155**, 276 (1912); **157**, 1364 (1913); **159**, 5 (1914); **166**, 94, 365 (1918); **168**, 357 (1919); **170**, 31, 1037 (1920); **171**, 1106 (1920); **172**, 893 (1921); **173**, 13 (1921); **175**, 1025, 1129 (1922). *J. de Phys.*, **5**, 1, 169 (1911). *Ann. de Chim. et Phys.*, **17**,437 (1909). *Revue de Mét.*, **19**, 90 (1922). A. de Gramont and G. A. Hemsalech, *Comptes Rendus*, **173**, 505 (1921); **174**, 365 (1922).

to construct tables of persistence suitable for the particular problem in hand. This will be explained below in discussing the value of this work. The essential thing is a knowledge of the sensitive rays and the ultimate rays, and these, as determined by de Gramont, are given in Table XXII.

De Gramont, in his work, used two spectrographs, one with lenses and prisms of uviol glass and the other with optical parts of quartz. It is remarkable that many of the sensitive lines lie within the region of the spectrum transmitted by uviol glass, that is to say, the region with lower wave-length limit of 3170 A. Indeed, it is possible in the great majority of cases to use only a uviol glass spectrograph, and this is important when expense has to be considered. The instruments actually used by de Gramont were the Hilger spectrographs illustrated in Vol. I., Figs. 62 and 64, pages 118 and 119.

In Table XXII. the elements which were investigated are arranged in alphabetical order, the lines of each element being divided into three groups, namely, those observed with a direct vision spectroscope, those photographed with the uviol glass spectrograph, and those photographed with the quartz instrument. The greater number of the lines given in the table were published in 1920.[1] Some of the results then set forth were amended by subsequent work, and I am indebted to Mr. Twyman for permission to include the later values here.[2]

The wave-lengths in I.A. of the ultimate lines are expressed in heavy type, and the most persistent of all are indicated by the symbols u_1, u_2, u_3, the last line to disappear being designated by u_1.

The identification of the sensitive and ultimate lines, representing, as it does, the result of fifteen years' work, may be accepted with complete confidence. It will be noted that there are certain points of difference between these values and those published by Hartley, by Pollok, and by Leonard, that is to say, the latter do not always agree as to which of the sensitive lines are the most persistent. On the whole, however, there is a remarkable agreement between the results obtained by the French and the English observers.

De Gramont, in some of his papers, has discussed in detail the application of his investigation to both qualitative and quantitative analysis. In both directions this spectroscopic method can be, and indeed has been, proved to be of very great value. In the case of qualitative analysis of complex minerals and of alloys, for example, it renders signal aid to the mineralogist and chemist. The delicacy of the method far transcends that of the ordinary chemical tests. As regards the technique, the alloy or mineral, if it conducts electricity, is sparked in the usual way. If the mineral is a non-conductor it may be fused with anhydrous sodium carbonate in a small platinum capsule and the spark spectrum of the melted material examined. By the use

[1] *Comptes Rendus*, **171**, 1106 (1920).

[2] These later values were communicated by Comte de Gramont to Mr. Twyman, and are published on pp. 81 to 84 of *Wave-length Tables for Spectrum Analysis*, by F. Twyman (Adam Hilger & Co., London, 1923).

TABLE XXII.

Sensitive and Ultimate Lines.

	Direct vision spectroscope.	Uviol glass spectrograph.	Quartz spectrograph.
Aluminium .	6245·1 6233·8	**3961·5** **3944·0**	3092·7 3082·2
Antimony .	——	3267·5 3232·5	**2598·1** **2528·5** 2311·5
Arsenic . .	——	——	2860·5 **2780·2** 2745·0
			2349·8 2281·1
Beryllium .	——	3321·4 3321·1	**3131·1** **3130·4** 2650·6
Barium . .	5535·5	**4934·1** **4554·0** 3891·8	2335·3
Bismuth . .	4722·5	——	**3067·7** 2989·0 2938·3
			2898·0 2780·5
Boron . .	——	3451·2	**2497·7** **2496·8**
Cadmium .	6438·5 5085·8	3610·5 3261·1	2748·6 **2288·0** **2265·0**
	4800·0		2144·4
Cæsium . .	——	**4593·2** 4555·3	. ——
Calcium . .	——	**4226·7** **3968·5** **3933·7**	3179·3 3158·9
Carbon . .	——	4266·9	**2478·6** 2296·9
Celtium . .	——	——	2685·2
Cerium . .	——	4186·6 **4040·8** **4012·4**	——
Chromium .	5208·4 5206·1	4289·7 4274·8 **4254·3**	——
	5204·5	**3593·5** 3578·7	
Cobalt . .	5353·5 5342·7	3474·0 **3453·5** **3405·1**	**2388·9** **2378·6** 2363·8
	5266·5	3395·4	2311·6 2307·9 2286·2
Copper . .	5218·2 5153·3	**3274·0** **3247·5**	——
	5105·6		
Urbium . .	——	3906·3 3692·7 3499·1	——
Europium .	——	4205·1 **4129·8**	——
Gallium . .	——	**4172·1** 4033·0	——
Germanium .	——	**3269·5**	**3039·1** 2651·6
Gold . .	6278·2 5837·4	——	2802·2 **2676·0** **2428·0**
	4792·6		
Hydrogen .	**6562·8**	——	——
Indium . .	——	**4511·4** **4101·8**	——
Iridium . .	——	**3513·7** 3437·1 **3220·8**	——
Iron . .	4404·8 4383·6	4045·8 3820·4 3737·1	**2755·7** **2749·3** **2739·6**
		3734·9 3570·2 3565·4	**2395·6** **2382·0**
Lanthanum .	——	4333·8 4086·7 3995·8	——
		3988·5 **3949·1**	
Lead . .	5608·9 5005·5	**4057·8** **3683·5** 3639·6	2614·2 2203·6 2175·8
Lithium . .	**6707·9**	**4602·2** 3232·7	——
Lutecium .	——	——	2963·3 **2911·4** 2900·3
			2894·9
Magnesium .	5183·6 5172·7	3838·3 3832·3	**2852·1** **2802·7** **2795·5**
	5167·3		
Manganese .	4823·6 4783·5	4034·5 4033·1 **4030·8**	2605·7 **2593·7** **2575·2**
	4754·1		
Mercury . .	5460·7	4358·3	2967·3 **2536·5**
Molybdenum .	5570·5 5533·2	**3903·0** **3864·1** **3798·3**	——
	5506·5	3635·2	
Neodymium .	——	4303·6 4177·3 3951·2	——
Nickel . .	5476·9 5081·1	3619·4 3524·5 3515·1	2437·5 **2416·2** **2316·1**
	4714·4	**3414·8** 3380·6	2303·0
Niobium . .	——	4101·0 **4079·7** **4059·0**	——
		3358·4	
Palladium .	5547·0 5295·6	**3634·7** **3609·6** 3421·2	——
	5163·8	**3404·6**	

TABLE XXII.—*Continued.*

	Direct vision spectroscope.		Uviol glass spectrograph.			Quartz spectrograph.		
Phosphorus .	——		——			2555·0	2553·3	2535·6
						2534·0		
Platinum . .	5475·8	5390·8	3966·4	3923·0	3268·4	3064·7	2929·8	2659·4
	5301·0	5227·6						
Potassium .	7699·0	7669·4	4047·2	4044·2	3447·4	——		
	5832·0	5801·8		3446·4				
	5782·4							
Radium . .	——		(4825·9	4682·2	3814·5)[1]	——		
Rhodium . .	——		3799·3	3692·4	3658·0	——		
			3434·9					
Rubidium .	7947·6	7800·3	4215·6	4201·8		——		
Ruthenium .	——		3499·0	3436·7		——		
Scandium .	——		4246·9	3651·9	3630·8	——		
			3613·8					
Silicon . .	6370·9	6346·8	3905·5			2881·6	2528·5	2516·1
						2506·9		
Silver . .	5465·5	5209·1	3383·0	3280·7		2437·7		
Sodium . .	5895·9	5890·0	3303·0	3302·3		2852·8		
Strontium .	——		4607·3	4305·5	4215·5	——		
			4077·7					
Tantalum .	6045·5	5997·4	3631·9	3406·9	3318·8	2963·3		
			3311·2					
Tellurium .	——		——			2769·8	2530·8	2385·8
						2383·3		
Thallium . .	5350·5		3775·7	3519·2	3229·8	2767·9		
Thorium . .	——		4019·1	3601·1	3539·6	——		
Titanium (green group) . .	5014·3	4981·8	3372·8	3361·2	3349·4	——		
Tin . .	4525·7		3801·0	3330·6	3263·3	2863·3	2840·0	2706·5
			3175·0					
Tungsten . .	——		4302·4	4294·7	4008·8	2397·1		
			3613·8	3215·6				
Vanadium .	——		4408·5	4379·2	3185·4	3118·4	3110·7	3102·3
			3184·0	3183·4		3093·1		
Ytterbium .	——		3988·0	3694·2	3289·4	——		
Yttrium . .	——		3774·3	3710·3	3633·1	——		
			3600·7	3242·3				
Zinc . .	6362·3		4810·5	4722·2	4678·2	2138·5		
			3345·0					
Zirconium (blue group) . .	4815·6	4687·8	3496·2	3438·2	3392·0	——		

of known weights of mineral and alkali, an estimate of the relative proportions of the metallic constituents present in the mineral can be made. Alternatively, the flame spectrum of the mineral may be examined with the help of the oxy-hydrogen or oxy-acetylene flame.[1]

As regards the quantitative application of this method, it must not be thought that this can be general. This was recognised by Hartley, who found, for example, that the estimation of copper and

[1] See p. 59.

iron in a pyrites by spectroscopy was far more lengthy and troublesome than by the standard gravimetric methods. On the other hand, there are directions in which the spectroscopic method can be applied with great advantage and with great rapidity. De Gramont very fully investigated these possibilities and proved that the addition of a spectrograph to the equipment of the analytical laboratories would be of unquestionable advantage in many of the great industries, particularly in metallurgy. He describes, in some detail, extended work he carried out on steels, wherein he established the possibility of determining the amounts present of the various elements used in the manufacture of steels for special purposes, such as high-speed steels, steels for high explosive shells, for special machinery, etc. He found that the method is applicable to the recognition of practically every element used in these steels and to the estimation of the amount present to within a sufficiently narrow limit of accuracy.

He established the applicability of the method to the determination of the percentage amount present of aluminium, boron, chromium, cobalt, copper, manganese, molybdenum, nickel, silicon, titanium, tungsten, and vanadium. He was even able to utilise the method with complex steels containing chromium, nickel, tungsten, and vanadium, which he met with during his work.

The method is based on the spectrographic study of a number of steels of known composition containing different proportions of each element under investigation. Since the persistence of the spectrum lines of one element is not altered in any way by the presence of other elements, one sets up in this way a series of standards for each element concerned. By simple comparison of the spectrum photograph obtained by sparking a steel of unknown composition with these standards the percentage amounts of the elements alloyed with the iron can at once be fixed with surprising accuracy.

It is obvious that once the standards have been set up the examination of a given steel by this method is extremely rapid. Particularly would this be true in the daily routine examination of the steels produced in a foundry, when the variations in content of certain known elements would not be large.

In addition to the elements given above, it is also possible to deal with carbon, phosphorus, arsenic, and tellurium, but the sensitivity of their lines is not greater than that given by the ordinary gravimetric methods. Very valuable information may, however, be gained by making use of these lines as a control when a large number of elements are present in the steel.

De Gramont gives as examples five steels wherein he was able to determine the amounts present of the metals to within a close approximation to the true value. The chemical analyses are set forth in Table XXIII., the quantities found being expressed in percentages.

TABLE XXIII.

	C.	Si.	Mn.	S.	P.	Cr.	W.	Ni.	Mo.	Va.	Cs.	Ti.	Cu.
I.	0·650	0·190	0·095	0·018	0·016	5·100	16·995	—	1·465	0·520	—	—	—
II.	0·34	0·28	0·61	0·017	0·022	0·48	—	0·99	—	—	—	—	—
III.	0·64	0·10	0·25	0·017	0·022	4·63	17·50	—	—	1·42	5·41	—	—
IV.	0·08	0·30	0·42	0·005	0·007	0·13	—	0·34	—	—	—	0·94	—
V.	0·70	0·28	0·50	0 04	0·04	1·41	—	2·11	—	—	—	—	0·17

The Mechanism of the Spark.—Before leaving the subject of spark spectra, a brief reference may be made to some investigations which have been made of the phenomena associated with the discharge itself. These investigations are of considerable interest in that they have thrown light on the actual mechanism of the spark. The first work which comes under review was carried out by Schuster and Hemsalech,[1] "On the Constitution of the Electric Spark," who studied the mechanism in the following way: Instead of a stationary photographic plate they employed a film which was moving at the rate of from 90 to 100 metres per second in a direction perpendicular to the spectrum lines; in this way it became possible to detect how the spark passes. It was then found on taking such a photograph of a spark that the air lines appeared perfectly straight, showing that the duration of this portion of the discharge was very rapid compared with the motion of the moving plate. They further found that the metal lines were due to oscillatory discharges, and were all curved so that they must start from the electrodes and travel with decreasing velocity towards the centre, the speed being calculable from the curvature of the lines; also it was noticed that this metallic discharge takes place after the discharge through the air. The mechanism thus is evidently as follows: The spark first passes extremely rapidly through the air, a single discharge; this vaporises the metal, which then spreads across the spark gap, conveying the current. The velocity of travel of the metallic vapour varies with different metals from 1300 to 400 metres a second, and appears to be quicker with metals of low atomic weight, but it varies for different lines of the same metal.

Schuster and Hemsalech also investigated the effect of introducing self-induction into the circuit, and they found that the air lines then disappeared from the spectrum, if the self-induction were great enough. This part of the work has been continued by Hemsalech,[2] who found that, in addition to removing the air lines from the spectrum of the spark, the self-induction also caused certain new lines to appear, and rendered the spectrum lines generally much narrower; he was able, for instance, in the case of hydrogen under atmospheric pressure, to obtain the spectrum lines as sharp as they are obtained in a vacuum

[1] *Phil. Trans.*, **193**, A, 189 (1900). [2] *Comptes Rendus*, **122**, 285 (1899).

tube. This narrowing of the lines produced by the introduction of self-induction in the circuit is of considerable use in certain cases, for example, in work upon the Zeeman effect, when, of course, for the best resolution it is necessary to have the spectrum lines as fine and narrow as possible. A self-induction coil may be made quite readily by winding wire round a bobbin, the coil being put direct in the circuit. Hemsalech, in some of his experiments, used a coil 50 cm. long, 5 cm. internal diameter, containing eight layers of wire, each consisting of one hundred and fifty turns.

Schuster and Hemsalech's work on the mechanism of the spark was taken up again by Schenck,[1] who obtained some very interesting results. Schenck investigated the action of self-induction, particularly in the case of the spark spectrum of cadmium. The apparatus consisted of a large induction coil fed with an alternating current, and a spark length was obtained of from 6 to 8 mm. with six one-gallon Leyden jars in the circuit. The period of the condenser was found to be $1{\cdot}3 \times 10^{-6}$ secs., and each spark consisted of ten or twelve complete oscillations. A large size Rowland grating was employed for the spectrum photographs. The cadmium spectrum was examined between the limits of $\lambda = 3700$ and $\lambda = 2100$, and it was found that the lines could be divided into three groups: A, B, and C. Group C consists of one hundred and forty lines about 0·3 A.U. wide with hazy edges; they resemble air lines, but are absent from other spark spectra. They extend only about 2 mm. from the poles, whilst the remaining lines extend right across the spark gap. They disappear when the condenser period is raised to 17×10^{-6} secs. by throwing in self-induction. Lastly, they are not present in the arc spectrum, and are not reversed. A similar group was found in the spectrum of zinc.

Group B contains most of the remainder of the lines known as "spark lines," that is, lines prominent in the spark and weak in or absent from the arc. They are not reversed; when the condenser period is increased to 75×10^{-6} secs. some of these lines disappear and the others shorten up to the poles, while the rest of the metallic lines extend uniformly across the spark gap.

The lines of group A are the so-called "arc lines," that is, those lines common to the arc and spark, their intensity being generally greater in the arc. They thus form a spectrum simpler than that of the arc, and the effect of self-induction is to make the spectrum of this group more complicated and approach that of the arc. The greater the period of the condenser the nearer is the approach to the arc spectrum. These lines extend right across the spark gap when the condenser period is great enough to shorten the lines of group B close up to the poles. They undoubtedly are due to luminous metallic vapours extending across the entire spark gap.

It would seem very possible that the B and C groups of lines have

[1] *Astrophys. Journ.*, **14**, 116 (1901).

their origin in two different stages of ionisation of the atoms of cadmium and zinc, the C group belonging to the doubly-ionised atom.

Schenck also investigated the appearance of the spark in a rapidly revolving mirror. The appearance of the spark under these conditions presents three general features. First, a brilliant white straight line due to the first discharge, sometimes followed by one or two weaker straight lines at intervals of half the complete condenser period. Second, curved lines of light which shoot out from the poles towards the centre with a continually diminishing velocity; when a streamer advances from one pole, the other pole is quite dark. Third, a faint light, generally of a different colour from the streamers, which fills up the spark gap and persists for a certain length of time after the oscillations die out. Now, the air lines are produced by the first straight line discharge, as Schuster and Hemsalech have already shown; the origin of the other lines (groups A and B) Schenck discovered by observing the spark in a rotating mirror, set at one time with its axis perpendicular to the spectrum lines and at another time parallel to them. From measurements of the plates the times of duration of certain lines were calculated, and these are given in Table XXIV.

TABLE XXIV.

	Wave-length.	Character.	Duration.
Magnesium.	4481	Strong spark line.	24×10^{-6} secs.
,,	3838		
,,	3832	,, arc triplet.	46×10^{-6} ,,
,,	3830		
Zinc.	4925	Strong spark lines.	14×10^{-6} secs.
,,	4912		
,,	4811	,, arc lines.	24×10^{-6} ,,
,,	4722		
Cadmium.	4800	Strong arc lines.	36×10^{-6} secs.
,,	4678		
,,	4416	,, in spark.	18×10^{-6} ,,

If anything, in this table the duration of the arc lines are underestimated; it is clearly shown how much longer the arc lines last than the spark lines. Schenck further found that the spark lines or those belonging to group B are due entirely to the curved streamers in the spark, but some of the spark lines are only to be found in the first few streamers. The lines of group A or the arc lines are partly due to the streamers, but a large part of their luminosity is due to the glow which persists throughout the spark gap after the streamers cease. This glow is undoubtedly due to metallic vapour distributed

over the spark gap. Schenck formed the opinion that the curved streamers do not carry the current, because an examination of the photographs shows that the streamers travel with a continually diminishing velocity, and that before they have reached halfway across the spark gap the whole discharge has passed and the return oscillation is beginning. It is also of importance to note that these streamers start from the negative electrode. For the velocity of the streamers Schenck obtained an initial value of 2·5 km. per second, in the case of the magnesium line at $\lambda = 4481$, which falls to about 1·7 km., about a millimetre out from the pole.

A simple method for the study of the spark was devised by Hemsalech,[1] who employed wedge-shaped electrodes set up in the same vertical plane, and at a slight angle to one another. On the top of each was fastened a small platinum wire, which just projected beyond the edge of the electrode in each case. From 3 to 6 mm. above the electrodes was mounted a glass tube 3 mm. in diameter, which directed a current of air through the space between the wedge-shaped edges of the electrodes. A steady current of air was maintained through this tube, and it was found that the several oscillations in each spark became separated, and appeared at different distances below the two platinum points. The initial discharge passed between the two points, so that the appearance of the discharge was a very fine, bright, straight spark between them. Below this was seen a series of large, curved sparks. Hemsalech was able to obtain as many as sixteen different oscillations, of which six to ten were quite fixed and regular. The velocity of the air in one of Hemsalech's experiments was 36 metres per second.

In a later paper Hemsalech [2] described the spectra of the initial spark and the subsequent oscillations, and as the former showed the line spectrum of air, and the subsequent discharge the band spectrum, he concluded that the initial discharge passes through non-ionised air, and the oscillations through ionised air.

Some further work has been carried out on this subject by Milner [3] and by Royds.[4] Part of Milner's work was concerned with the nature of the streamers. In order to find out whether these streamers consist of charged particles or not, he observed by means of a rotating mirror the spark which was made to pass across a powerful magnetic field. The displacement of the streamers that were then observed proved conclusively that the particles composing these streamers must be electrically charged. Royds dealt more especially with the velocity of these streamers and the variation in intensity and velocity caused by self-inductance. All the lines of the same spectrum do not indicate the same velocity, but they may be divided into two classes, long lines indicating normal velocity and short lines indicating a larger

[1] *Comptes Rendus*, **140**, 1103 (1905). [2] *Ibid.*, **141**, 1227 (1905).
[3] *Phil. Trans.*, **209**, 71 (1908).
[4] *Ibid.*, **208**, 333 (1908); and *Phil. Mag.*, **19**, 285 (1910).

velocity. The velocity of the lines of the first type is probably due to diffusion, but that of the second type is too large to be explained in this way. Some of Royds' observations are given in Table XXV.

Mohler [1] photographed the spectrum of the spark looking at it end on, in order to see if the rapidly moving particles in the streamers caused any displacement in the position of the lines in the spectrum owing to what is known as the Doppler effect. The electrodes were of different metals, and a photograph was taken looking along the spark in one direction, and then without disturbing the plate the spark was rotated through 180° and a second photograph taken. In this way the effect, if any, would be doubled, as at the one time the particles would be moving towards the slit, and at the other time away from the slit. The actual effect that was observed was very small, corresponding to a velocity of 0·37 km. per second for the lines of aluminium at $\lambda = 3961$ and $\lambda = 3944$; an actual displacement of the lines of 0·1 A.U. was observed on the plates. The displacements of certain iron lines were slightly smaller, as also were those of some magnesium lines. The cadmium lines at $\lambda = 4078$ and $\lambda = 4800$ gave a slightly greater velocity. The line which gave Schenck a velocity of 2·5 km. per second could not be measured properly, as it was too wide and shaded. Doubtless, however, only an average velocity was observed, since according to Schenck the velocity falls to two-thirds of its initial value at 1 mm. from the electrode, it being extremely difficult only to photograph the spectrum of the very commencement of the spark. Mohler noticed a very interesting result in the fact that when the particles were leaving the slit the lines of magnesium at $\lambda = 2795$, $\lambda = 2802$, and $\lambda = 2852$ were strongly reversed, just as the last line is reversed in the arc; this was not observed when the particles were approaching the slit.

The Spectra of Gases.—The production of luminescence in gases is very different from the methods which have been described previously. The manipulation of gases and the filling of the tubes used for their excitation constitute a branch of work with a technique which is all its own, and requires on the part of its followers patience and an understanding of the vagaries of Dame Nature in her most capricious moods. Although some observations have been made of the spectra of gases at atmospheric pressure, such, for instance, as that of air, the most usual method of excitation is the passage of a high potential discharge between two electrodes sealed in the walls of a tube which contains the gas under low pressure. The filling of these discharge tubes, which by common consent are called vacuum tubes, involves numerous difficulties, not the least of which is the insistent prevalence of impurities which arise from the electrodes and from the walls of the vacuum tubes. The preparation and filling of vacuum tubes thus involve rigid precautions being taken against all sources of contamination, because the quantity of the gas under

[1] *Astrophys. Journ.*, 15, 125 (1902).

TABLE XXV.

VELOCITIES OF THE METALLIC VAPOUR IN METRES PER SEC. CAPACITY = 0·0306 M.F.D.

Self-inductance (calculated)	0·000014 henry.	0·00025	0·00073	0·0025	0·0043	0·0068	0·0124
Period . .	0·388 × 10⁻⁵ sec.	1·65 × 10⁻⁵	2·98 × 10⁻⁵	5·5 × 10⁻⁵	7·2 × 10⁻⁵	9·05 × 10⁻⁵	12·25 × 10⁻⁵
Magnesium .	930 m./sec.	416	390	—	378	381	226
Calcium . .	551 165	590 102	582 —	376 139	400 108	— 121	— 97
Mercury . .	936 1155	594	616	518	—	—	—
Lead . .	345	—	282	280	—	—	—
Bismuth . .	303	534	224	—	—	—	—
λ 4260 .	—	615 for the same distances from the electrodes.	—	—	—	—	—
λ 4561 .		1170					

examination in the tubes is so small that minute amounts of impurities have a relatively great importance.

Certain observations have been made upon the spectra of gases at ordinary atmospheric pressures; sparks from an induction coil are passed between platinum wires in the gas, some form of tube being used as is shown in Fig. 49. The gas is enclosed over mercury in the tube *a*, which has two platinum wires sealed into the glass, between which the sparks pass. As will be explained more fully later, certain gases give different spectra according to whether or no a Leyden jar is put in the circuit; the condensed or uncondensed spark is therefore employed as may be required, but in the latter case the discharge should not be sufficiently strong to heat the electrodes red hot.

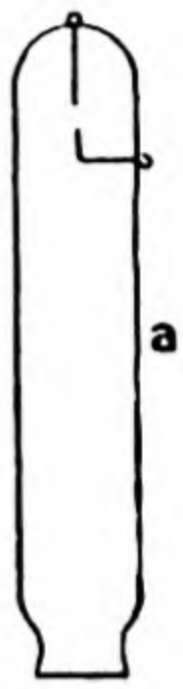


FIG. 49.

By far the most general method is to submit the gases under reduced pressure to the action of the discharge. Various shapes of tubes have been employed, of which the most useful are shown in Fig. 50, at *a*, *b*, and *c*.

The tube shown at *a* was first designed by Plücker, who found that when a capillary tube is placed between two wider portions the brilliancy of the illumination is enormously increased in the narrow portion. The forms *b* and *c* are arranged that the glowing gas may be observed through a quartz plate so that the ultra-violet rays may not be absorbed; in *b* the capillary portion is viewed "end on," and *c* is used in investigations of the glow round the electrodes. Many other designs have been produced according to the especial character of the work, but it will be found that for all ordinary investigations one of the above forms will suffice. Each of the tubes is shown provided with two electrodes; in certain cases these cannot be used, and then it is necessary to wrap the ends of the tubes with tin-foil, which is put in connection with the secondary poles of the induction coil. Alternatively, brass caps may be used which fit loosely on the ends of the vacuum tube, the space between the two being filled with finely-powdered graphite. It is not, I think, advisable to employ electrodeless tubes unless circumstances render it necessary, for although they are easier to make they are not so easy to fill; and further, they are rather inclined to give the enhanced line spectrum of the gas when one exists. A further objection to them is that they are liable to become pierced if the discharge is too powerful.

The following directions may be given for the making of a vacuum tube. The most important part of a vacuum tube is the electrode. Unless this is properly made it may, and generally does, become a never-ending source of trouble; it breaks to pieces, melts up, and then often cracks the tube. Except for special purposes, the electrodes themselves are usually made of aluminium wire; this is the most satisfactory, as, on account of its good conductivity, it does not readily become hot, and, therefore, is less inclined to melt. Platinum is sometimes used, but this always gets very hot, and, further, "evaporates"

very considerably; a mirror is deposited upon the walls of the tube immediately surrounding the electrode, this being particularly noticeable at the negative pole. When an aluminium electrode is used, it must be joined to a piece of platinum wire which can be sealed into the glass; the two wires can be quite easily fused together by heating the extreme end of the aluminium in a fine-pointed blow-pipe flame and gently pressing the platinum against it until it melts, when the platinum will just penetrate the aluminium. The junction is at once removed from the flame, and will be found to be quite strong. Before carrying out the operation it is advisable to cut both the aluminium and platinum wires to the required length; each of them may then be held in a pair of tweezers or small pliers, and will be found much easier to manipulate. After the junction has been

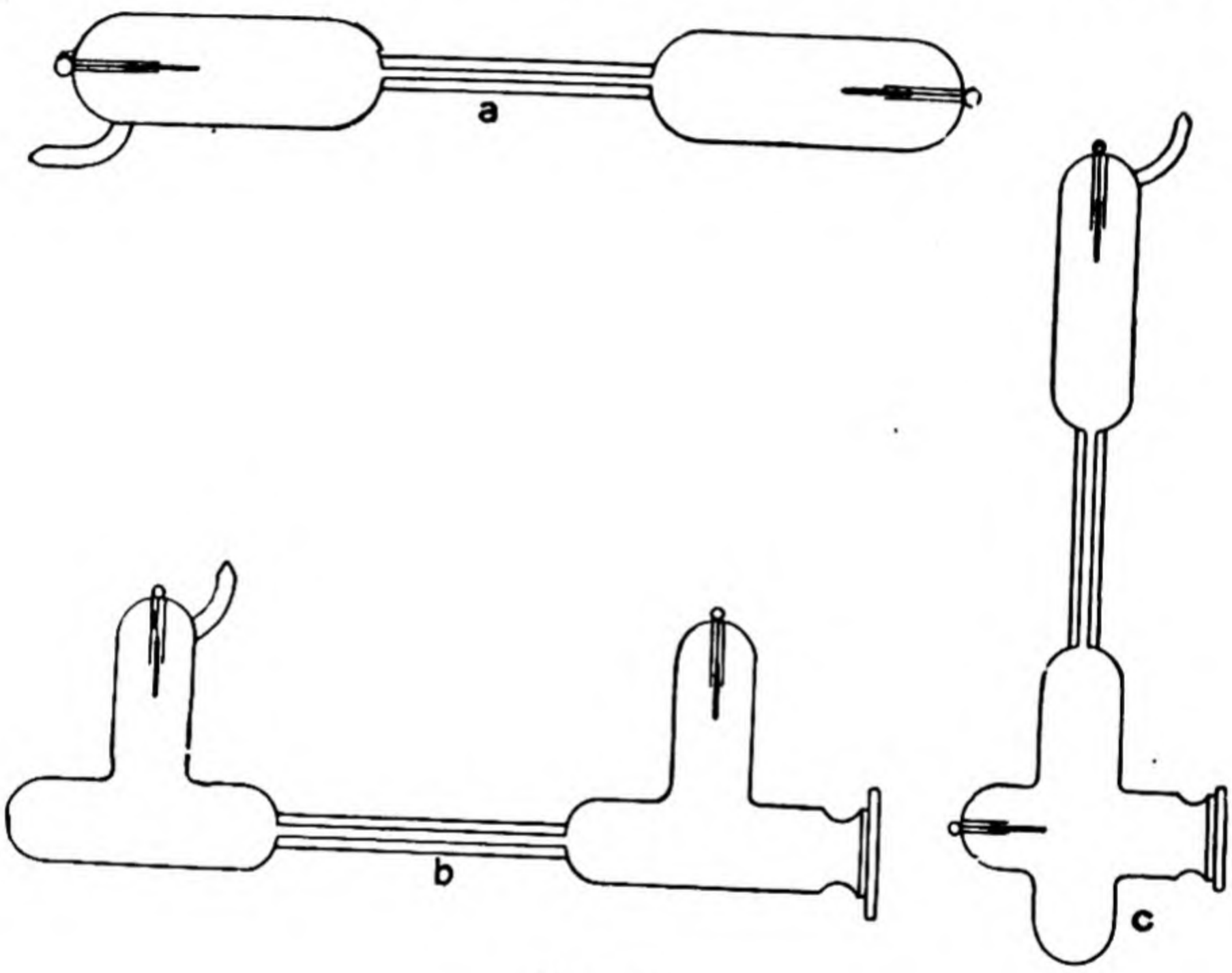


FIG. 50.

made, it is necessary to protect the platinum wire by a glass cover, so that no discharge can take place from any portion of its surface. A piece of fine quill tubing is made in the blow-pipe with a bore sufficiently large just to pass over the aluminium wire; if, at the junction of the platinum and aluminium, there are any lumps which prevent this cover from slipping over it, they may be removed by filing. The electrode, with its cover, is shown in Fig. 51 at *a*; the next step is to melt down the glass cover on to the platinum, as shown in *b*, using a fine-pointed flame. A small quantity of blue enamel glass is then melted round the end of the platinum, as shown at *c*, care being taken that the enamel and the ordinary glass are well fused together, and that the enamel portion is larger than the rest. The use of the enamel lies in the fact that it is not possible to seal platinum into

ordinary German glass without the joint cracking on cooling, owing to the great difference between the coefficients of expansion of the platinum and glass. The enamel glass has a coefficient of expansion midway between the two, and platinum can thus be sealed in quite safely with its aid. English lead glass, on the other hand, needs no enamel, but it is very much more difficult to work, owing to the liability of the lead oxide to be reduced to lead. Some enamels are made of lead glass, but in my opinion they are not so satisfactory as the blue soda variety.

The electrode is now ready for sealing into the tube. The previously rounded end of the tube has a small hole blown in it, which is then filled with enamel, and the whole melted down and blown out until quite even and round. A hole is then made in the enamel end of the tube, into which the electrode is placed, and the enamel lump on the latter is carefully melted to the edges of the hole, and then the seal is several times melted down and blown out until a good junction is obtained. The three stages are shown in Fig. 52; *a* is the tube with the enamel melted into the end; *b*, the same with a hole blown in the enamel end, and the electrode resting on the edges; and *c*, the finished junction. In all three the enamel is represented by the shaded portion; the preparing of the end of the tube by melting in a little enamel previous to the sealing of the electrode is a very necessary proceeding, a better joint being always obtained in this way.

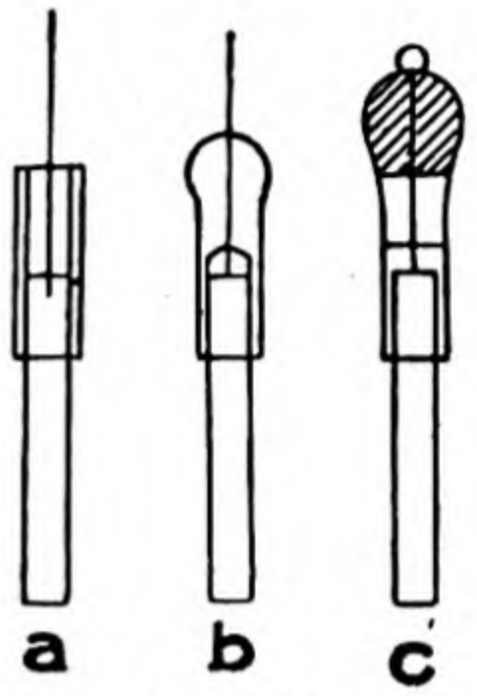


FIG. 51.

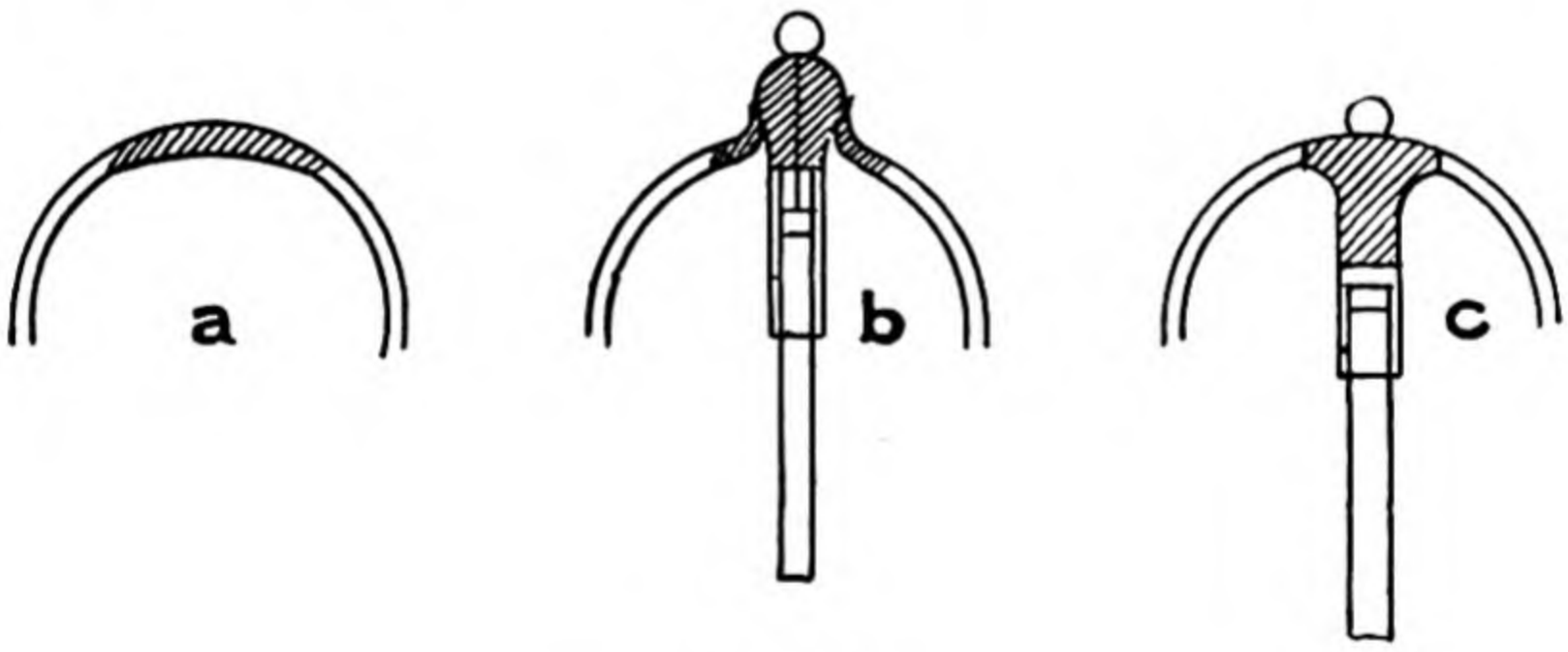


FIG. 52.

It will be found that electrodes prepared in this way will answer perfectly satisfactorily for all ordinary gases; if they are to be used with very strong currents, the aluminium wire should be rather thick; Nos. 16-18 S.W.G. are very convenient sizes.

The monatomic gases, neon, krypton, etc., require a little alteration in the electrode if one wishes to pass the current continuously for long periods. For some reason even aluminium electrodes get very hot with these gases, and therefore they must be more carefully made,

to prevent their rapid disintegration.[1] Stout aluminium wire of at least No. 12 S.W.G. is taken, and from one end along the axis a fine hole is bored for a short distance. Into this the platinum wire is placed, and the aluminium pressed on to it with a pair of pliers; the platinum is held quite firmly in this way. The glass cover-piece is made by making some capillary tubing out of the enamel glass and joining it on to a piece of ordinary glass tubing, as shown in Fig. 53, with the electrode lying in its place. The enamel is melted on to the platinum at the extreme end, *a*, which must be at least half an inch from the aluminium, after which the electrode is finished off in the usual way.

A very important precaution that must be taken is the thorough cleansing of the glass of the vacuum tube; this must, of course, be seen to before the electrodes are sealed in, and should be done by filling the tube full of hot chromic acid (potassium bichromate and strong sulphuric acid) and allowing it to stand for a short time; after which it is thoroughly rinsed with distilled water and dried. The tubing from which the vacuum tube is made should also be cleaned before it is used.

The process of filling a vacuum tube with a gas may be carried out by means of the apparatus diagrammatically shown in Fig. 54, where

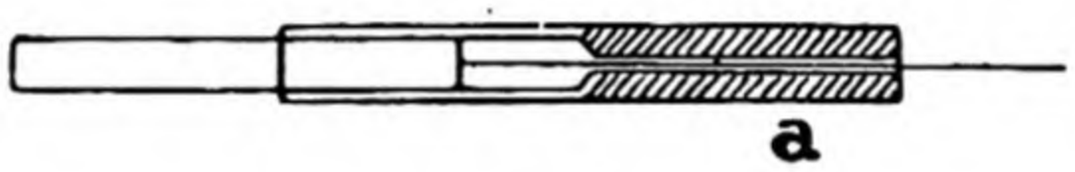


FIG. 53.

A is a mercury air-pump which is connected to the apparatus for filling through the drying tube *a*, containing phosphorus pentoxide, and the stopcock *b*. The apparatus for filling is shown at B, and the vacuum tube at C. The former consists of a bulb, *c*, with four branch tubes, one of which leads to the stopcock [2] and inverted syphon *d*; a second connects through the drying tube *e* (phosphorus pentoxide) to the stopcock *f*; the third and fourth respectively lead to the stopcocks *b* and *g*. The vacuum tube C is joined through a constricted portion, *h*, to the stopcock *f*; the inverted syphon *d* dips into mercury in a glass trough as shown. It is far preferable that in an apparatus such as this all the joints should be sealed with the help of a hand blow-pipe to ensure the absence of any leaks; the side branches at *k*, *k* are for the purpose of blowing in during such sealings. Over the end of the inverted syphon *d* is placed a tube, *i*, containing the gas required for the experiment; such tubes of gas are conveniently kept standing in mercury in a porcelain crucible, as shown at *l*.[3] This gas

[1] Baly, *Phil. Trans.*, **202**, A, 183 (1903).

[2] It may not be out of place to give a good lubricant for stop-cocks, which may be made as follows: 2 parts of soft rubber and 1 part of vaseline are melted together, and then one-eighth part of paraffin wax is added, and the whole well stirred. The mixture is then allowed to cool.

[3] For a full description of the modern methods of gas manipulation, see *The Study of Gases*, M. W. Travers. Macmillan & Co., 1901.

can thus be admitted into the exhausted apparatus by depressing the tube *i* until the end of the syphon is in the gas, and then opening the stopcock *d*. It is necessary, therefore, for the inverted syphon to be full of mercury before the gas is admitted, and this is the first step.

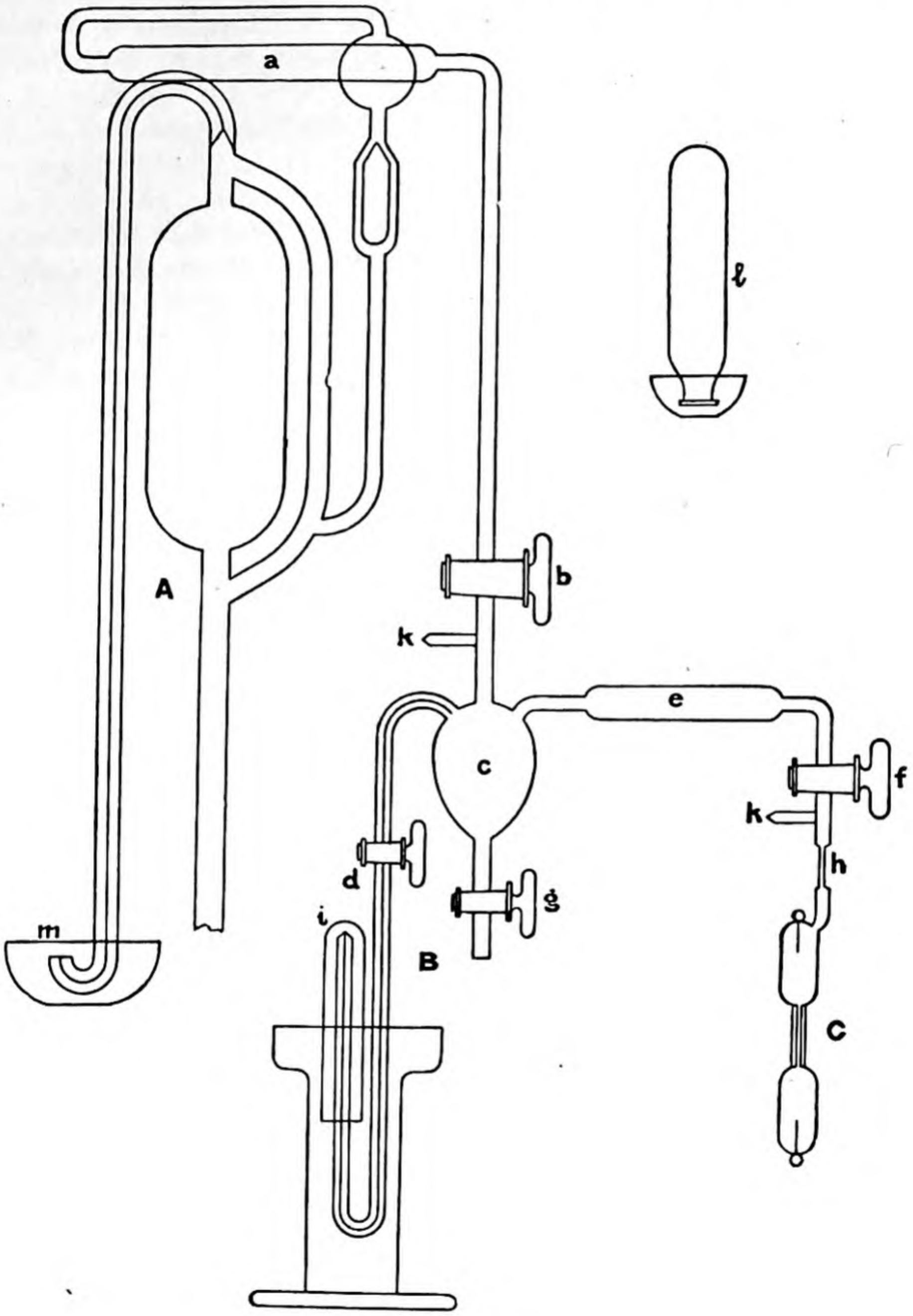


FIG. 54.

to be taken in the process of filling a vacuum tube. When the apparatus has been partially exhausted, the stopcock *d* is slowly opened with the end of the syphon under the mercury ; the mercury runs in, and is allowed just to rise above the stopcock, when it is again closed.

The whole apparatus is now thoroughly exhausted, and the current from the secondary of an induction coil (the same size as will be afterwards used in connection with the tube) is passed through the vacuum tube. There are certain sources of contamination in every vacuum tube which must be removed if a pure spectrum be desired, before the gas can be admitted; these are, moisture on the glass walls and on the electrode, a small quantity of hydrogen apparently occluded in the aluminium electrodes, and sometimes dirty glass surfaces. The first two are almost entirely sources of hydrogen, and the last of carbon dioxide.

It is the last which gives the greatest trouble, but it may be entirely got rid of by carefully cleaning the tube with chromic acid during its making, as previously directed. We need, therefore, only concern ourselves with the first two sources of trouble; these may be removed by continuing the exhaustion while the discharge is passing until the hydrogen ceases to be evolved. This, as a rule, does not take long, and is considerably hastened by passing a strong current and by carefully heating the tube with a Bunsen flame. The exhaustion should be carried to as high a degree as possible; that is to say, until the tube shows brilliant green phosphorescence or until the discharge refuses to pass. The spectrum of the discharge at any time may be examined with one of the plain direct-vision prisms described in Vol. I., p. 98. If the carbon banded spectra become visible, owing to there being carbon dioxide present, it will generally be found rather more troublesome to reach a sufficiently high exhaustion. Under these circumstances the tube should be heated as hot as possible, and, after the admission of a small quantity of air, re-exhausted; this being repeated until the carbon bands disappear. If they prove very obstinate, it will often prove of considerable help to close the stopcock *b*, and then fill the vacuum tube with air by carefully opening the stopcock *g*. If the tube be again exhausted, it will frequently be found that the carbon bands have disappeared.

Attention may also be drawn to the necessity of using perfectly pure phosphorus pentoxide in the drying tubes *a* and *e*; this substance must be free from lower oxides of phosphorus, which are very detrimental. A sample of the substance, when allowed to stand in the air, should be converted into a quite colourless mass of metaphosphoric acid, without any red or yellow spots.

When the vacuum tube has been exhausted, a small quantity of the required gas may be admitted; the stopcock *b* is closed, and the tube *i* is well pressed down over the inverted syphon; the stopcock *d* is then slowly opened, until the mercury just runs through. When a volume of mercury has passed equal in volume to the amount of gas required (which should be less than the total volume of the syphon), the tube *i* is raised so as to cover the end of the syphon with mercury. The gas then enters the apparatus, and is followed by a column of mercury; the stopcock *d* is closed when this second column of mercury begins to pass through it. It will generally be found that a

volume of gas occupying 2 or 3 inches of the capillary is sufficient; it is best to admit a little too much gas, and then slowly reduce the pressure, by opening *b*, until the best illumination is obtained in the vacuum tube. The tube may now be sealed off by carefully melting the constricted portion at *h* with a fine-pointed blow-pipe flame. If the gas is very valuable, it may be exhausted out of the residual apparatus through *b*, and collected at the end of the delivery tube of the pump at *m*.

When the vacuum tube spectra are required of the vapours of substances solid at ordinary temperatures, the special apparatus for filling is not necessary; some of the solid in question is put into the vacuum tube before sealing to the apparatus, and the tube is then sealed on in a horizontal position. When the tube has been completely exhausted, the substance is heated until it vaporises, and its spectrum is obtained; the exhaustion is continued for a short time to remove any gas which may have been occluded in the substance, and the tube is sealed off.

Certain substances necessitate special precautions being taken in obtaining their spectra; amongst these the following examples may be quoted. The monatomic gases—helium, neon, argon, krypton, and xenon—have, as mentioned above, the curious property of heating the electrodes very considerably in vacuum tubes, and this gives rise to the evolution of a second quantity of hydrogen.[1] If into a tube, which has been carefully exhausted in the manner described above, all the hydrogen possible having been removed, a small quantity of one of these gases be admitted, at once a further quantity of hydrogen is evolved in quite sufficient amount absolutely to mask the new gas spectrum. It is therefore necessary that this hydrogen be removed before the new gas spectrum can be obtained pure; this can only be done by the repeated admission of small quantities of argon and re-exhaustion, the process being repeated until the hydrogen lines disappear from the spectrum. Any one of the new gases would answer the purpose, but argon is at present the only one that we can afford to waste in this way. It is curious that this effect does not take place when the gases are not quite pure—that is to say, when they contain diatomic impurities; a further point of interest is that the process known as electrical evaporation of the electrodes takes place very rapidly with these gases when pure, the aluminium subliming and depositing a mirror on the glass walls immediately surrounding it. Again, these gases carry mercury vapour with them into the vacuum tube with great ease, so that its spectrum is very strong, sometimes even masking that of the other gas present. This, however, can be removed by keeping the discharge passing for some minutes through the tube, when apparently the mercury is absorbed by the electrodes.

The foregoing is a general description of the method which should be adopted in filling vacuum tubes with gases for the examination of

[1] Baly, *Phil. Trans.*, **202**, A, 183 (1903).

their emission spectra. It must be remembered, however, that in certain cases special methods must be adopted. It is not possible here to enter into the details of all these special methods, since so much depends upon the particular nature of the problem in hand. One or two instances may, however, be mentioned where simplifications have been introduced or where peculiar difficulties have to be surmounted. As an example of the former we may take the experimental arrangement adopted by Merton and Barratt [1] in their investigation of the secondary spectrum of hydrogen, which will be described in detail in the next chapter. These authors did not adopt the method described above to admit hydrogen into their discharge tubes, but they made use of the permeability of palladium to this gas. A short platinum tube was sealed into each vacuum tube, and this platinum tube was attached to one end of a palladium tube, the other end of which was closed. By heating this tube with a naked flame or in an atmosphere of hydrogen any desired quantity of this gas could be admitted.

Then, again, we have to consider such cases as the halogen elements which act on mercury, and, therefore, cannot be handled in the manner described above. With chlorine or bromine the simplest method is to use a metallic chloride or bromide which can be decomposed by the action of heat, a small quantity of the salt being placed in a side tube attached to the vacuum tube. When the vacuum tube has been thoroughly exhausted, the salt may be heated and the halogen evolved. The gold salts may be used as the chloride readily decomposes at about 250° C., and the bromide at about 120° C. In the case of iodine the free element may be placed in the side tube. Owing to the volatility of iodine at room temperature, it is advisable to guard against the passage of the vapour into the exhaust pump, especially if a mercury pump is used. This may partly be obviated by cooling the side tube during the preliminary exhaustion and clean-up of the vacuum tube. It is advantageous to introduce a guard tube containing silver leaf between the pump and the vacuum tube.

In all three cases the ordinary aluminium electrodes should not be used, as the stable halogen salts of this metal will be formed. As an alternative, platinum electrodes may be used, which are protected by an enamel coating, so as to leave only a very short length exposed, or, better still, electrodeless tubes may be employed.

A further trouble sometimes met with in vacuum tube work is the gradual disappearance of the gas under examination in the vacuum tube, owing to absorption, decomposition, polymerisation, or some such cause. In cases where one or other of these phenomena occurs it is advisable to maintain a slow and constant supply of the gas into the vacuum tube, the exhaust pump being kept in operation during the whole time. In order that the spectrum may be examined the apparatus is so arranged that the vacuum tube is mounted in the

[1] *Phil. Trans.*, A, 222, 369 (1922). See p. 203.

correct position opposite the slit of the spectrograph, an end-on form being used. The tube is then attached to the exhaust pump and to some form of apparatus whereby a slow and constant stream of the gas can be admitted. The most convenient method of securing the latter condition is a long fine capillary tube which is connected with a reservoir containing the gas. It is hardly necessary to point out that the rate at which the gas is admitted must be sufficiently slow to be within the capacity of the exhaust pump to remove, that is to say, the pump must be able to maintain the pressure sufficiently low for the correct discharge conditions to be secured in the vacuum tube.

It may be pointed out that it is not satisfactory to control the supply of the gas by means of a stopcock. Apart from the difficulty of adjustment there is the danger of contamination by the lubricant used, this being much greater when the stopcock is nearly closed than when it is fully open. In general, the use of stopcocks should be avoided as far as is conveniently possible, although in many cases, of course, it is necessary to use them.

Among the directions given above for filling a vacuum tube, it was briefly stated that the pressure exerted by the gas therein should be adjusted until the best result is obtained. The pressure of the gas often exercises a very considerable influence on the definition of its spectrum lines, and, further, on the relative visibility of the components of a gaseous mixture. An example of the first effect may be drawn from the monatomic gases, for unless the pressure lies within certain small limits the radiations become very ill-defined; this is true for krypton in the orange region, and particularly for xenon over the whole spectrum.[1] It was found in filling tubes with xenon that, unless the pressure was below a certain limit (which was not measured, but probably about 1 to 2 mm.), the lines, especially of the spectrum obtained with the Leyden jar in the circuit, were hopelessly confused, having in many cases a width of 6 to 8 A.U., and were seen upon a continuous background. When the pressure was slowly reduced, the continuous background disappeared, and the lines became in the end absolutely sharp. It will often be found in working with gases under reduced pressures that there is a definite pressure at which the best effect is produced.

The second effect of pressure, namely, the effect on the relative visibility of the components of a mixture of gases, is well shown by some results obtained by Collie and Ramsay with a mixture of helium and hydrogen.[2] With a mixture of two parts of hydrogen and one of helium, the latter was invisible at a pressure of 2·61 mm., but at a pressure of 0·43 mm. the helium spectrum was strong, and as the pressure was reduced it became stronger, until at 0·072 mm. the red line was as bright as the red hydrogen line; at 0·012 the helium spectrum was stronger than the hydrogen throughout. The same was true of

[1] Baly, *Phil. Trans.*, **202,** A, 183 (1903).
[2] *Proc. Roy. Soc.*, **59,** 257 (1896).

other mixtures of the same gases, it being found that the less helium in the mixture, the lower was the pressure necessary to make it visible. Generally speaking, therefore, the pressure is an all-important factor in spectroscopically testing a mixture of gases. Some interesting qualitative observations upon the spectra of mixed gases have been published by Nutting.[1] It has also been found that, when the discharge is passed through a mixture of two gases, they are separated, one appearing in the negative glow and the other in the positive column.[2] This phenomenon has also been observed by Merton and Barratt.[3]

A few words may be said about the various forms of pumps which are used in the exhaustion of apparatus, a process which forms a very essential part of many investigations in spectroscopy, and is by no means confined to vacuum tube technique. This, however, is a suitable opportunity to deal with this very important question. Pumps may be broadly divided into three classes, namely, the mercury pump, the mechanical pump, and the mercury vapour diffusion pump. It is worthy of note that the first idea of a mercury pump was formulated by Swedenborg, and the development of this class of apparatus from the initial form, in which, owing to rubber tubing being then unknown, it was necessary to pour in and draw off the mercury, to the types in use at the present day, forms quite an interesting chapter in the history of science. There are two types of mercury pump in common use, namely, the Toepler pump and the Sprengel pump. The former is shown at A in Fig. 54, on p. 164, but the mercury reservoir and the india-rubber pressure tubing connecting this to the vertical tube are not shown. The pump is operated by raising the reservoir until the mercury fills the pump-head and flows over down the capillary fall tube, the glass valve shown on the right preventing the mercury from passing over into the rest of the apparatus. When the pump-head is thus filled with mercury, the reservoir is again lowered until the mercury falls below the level of the side tube connecting with the apparatus to be exhausted. Care must be taken during the first few strokes of this pump to guard against lowering the mercury too rapidly, since the rush of air through the mercury into the evacuated pump head may break the pump.

The Sprengel pump is shown in Fig. 55, where A is the simple form and B is the form most suited for accurate work. In the latter the mercury first passes through an air-trap, shown in detail in C, and then is sprayed into an exhausted bulb before it enters the pump proper. The Sprengel pump has the disadvantage of being slow in its action at medium pressures, but is very efficient at low pressures. Either the Toepler or Sprengel pump must be used when it is desired to collect the gas which is pumped out of the experimental apparatus.

[1] *Astrophys. Journ.*, **19**, 105 (1904).
[2] Baly, *Phil. Mag.*, **35**, 200 (1893); J. J. Thomson, *Nature*, **52**, 454 (1895).
[3] *Phil. Trans.*, A, **222**, 369 (1922).

There are many forms of the mechanical pump, and of these a few only may be mentioned. There is first the Gaede rotary mercury pump, and the more recent molecular pump, the principle of which consists in the very rapid rotation of vanes within a circular chamber only a fraction of a millimetre larger than the vanes. Its efficient action at low pressures is due to the high viscosity of air. In this group are included the various designs of oil pumps of both reciprocating and rotary types. Of the latter type the Trimount and the Cenco

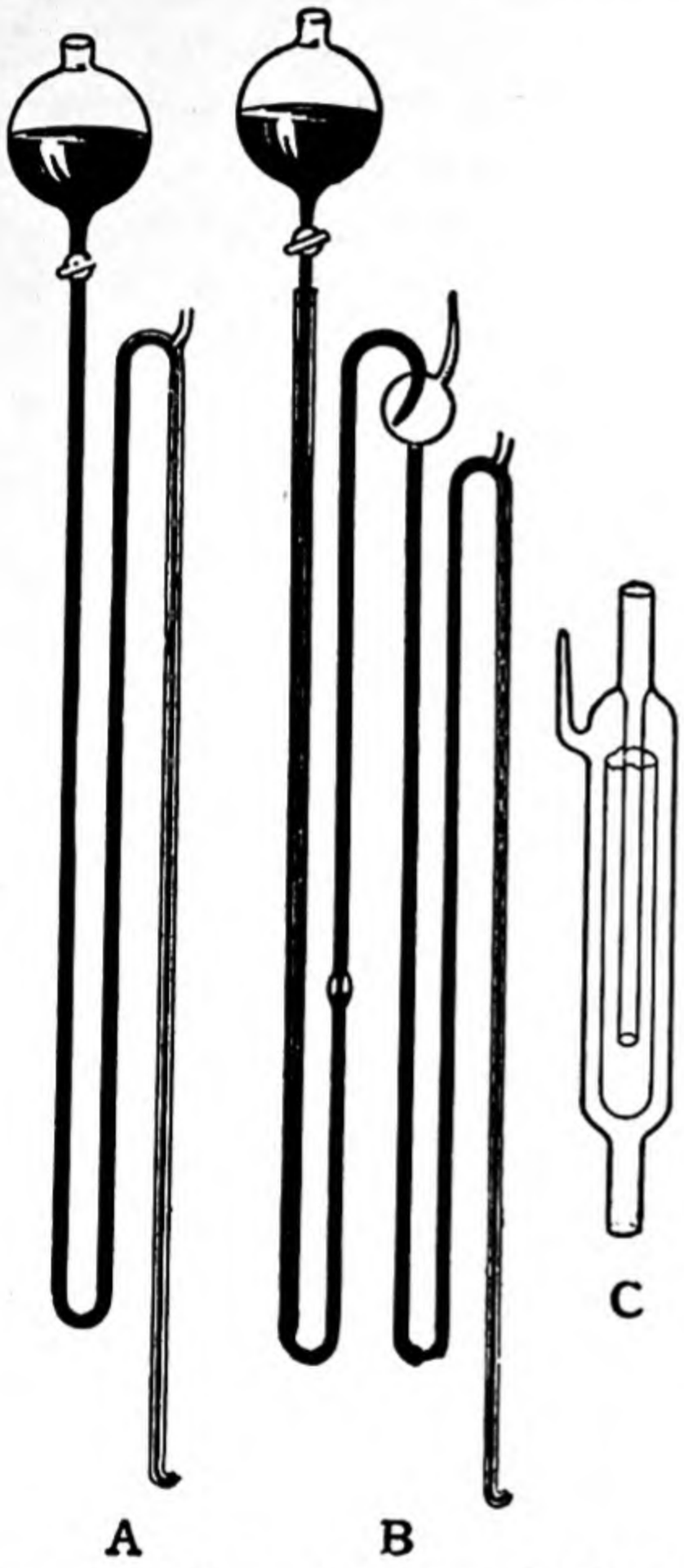


FIG. 55. (From Travers' *Study of Gases*. Macmillan & Co., Ltd.)

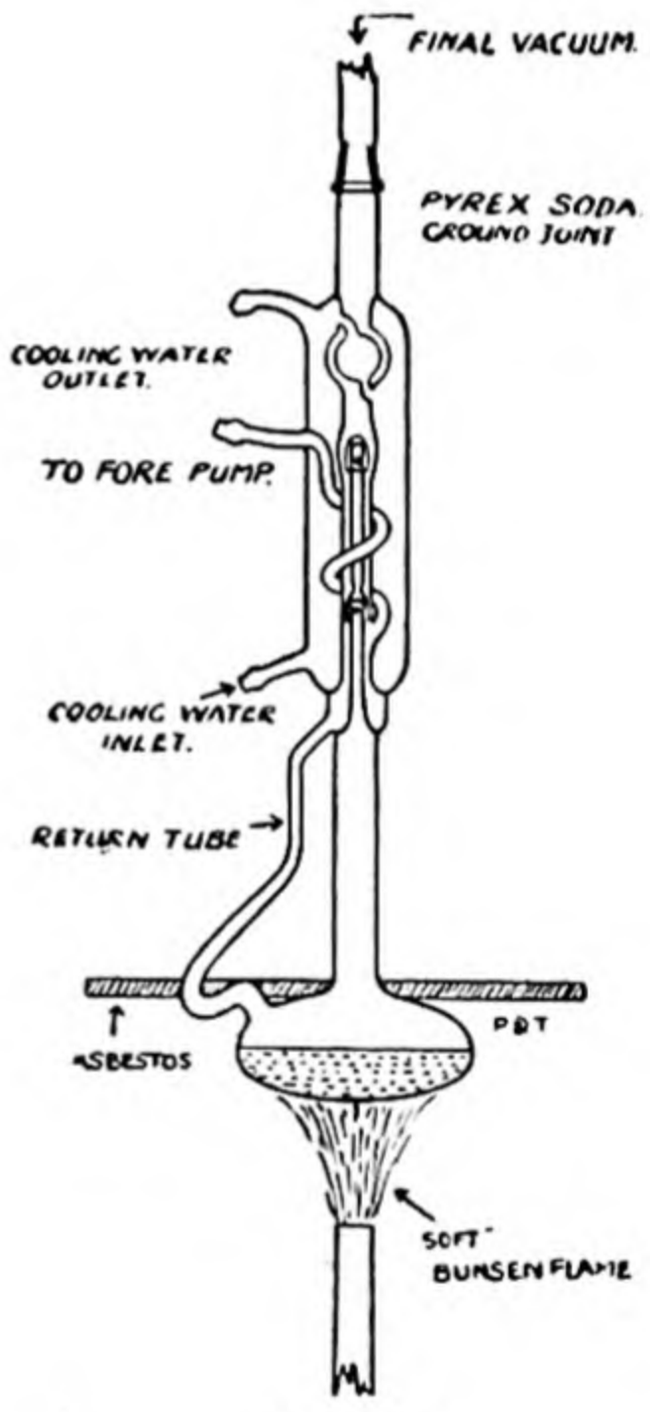


FIG. 56.

pumps may be mentioned as being highly efficient and satisfactory in their action.

There is a limit beyond which it is not possible to pass when the exhaustion is effected by any of the above pumps, this being due partly to the vapour pressure of the mercury or oil when such is used, and partly to the viscosity of air at very low pressure. The problem of obtaining very high vacua has been solved by the mercury vapour diffusion pump, which, by its action, causes a flux of gas from the exhausted chamber to the exhaust pump. One of these diffusion pumps is placed between the apparatus to be exhausted and some

form of mechanical pump. When the latter has reduced the pressure on the whole apparatus to 1 mm. or less, the diffusion pump is started, the mechanical pump being kept in action the whole time. One of the many designs of mercury vapour pumps is shown in Fig. 56.[1]

Two very useful adjuncts in the exhaustion of small pieces of apparatus have been described, one being the absorption of gases by heated calcium and the other the absorption by charcoal cooled in liquid air.

In the first method, which is described by Soddy,[2] the metallic calcium is placed in a small porcelain test tube inside an outer glass tube, the whole being surrounded by a shield tube of porcelain and heated in an electric resistance furnace. The glass tube is directly connected to the vacuum tube or apparatus to be exhausted. Soddy proved that calcium when heated absorbs all gases except helium, argon, and the other monatomic gases. Since the optimum temperature is above the softening point of ordinary glass, it would be preferable to use a hard glass tube which is connected to the rest of the soft glass apparatus by means of a ground glass joint.

The absorption of the gases is rapid, so that the method of exhaustion is exceedingly convenient. Care must, however, be taken not to heat the calcium to too high a temperature, because some of the substances which are formed, *e.g.* calcium hydride, will be liable to dissociate and evolve the gases which were absorbed at a lower temperature. The actual absorption takes place in a very short time, and if in practice it be found that the absorption when once started does not complete itself, it will be advisable to allow the temperature to fall and not to rise, so as to increase the stability of the dissociating compound. The natural tendency on finding that the gas is not entirely absorbed would be to increase the temperature, but Soddy points out that incomplete absorption is usually due to the temperature being too high. The great advantage of this method is that the tube containing the calcium and the furnace may be connected to the vacuum tube, there being no need for any drying tubes, so that the total volume of the apparatus is reduced to a minimum.

Some very interesting results were found by Soddy in the course of his experiments with the furnace owing to the fact, as stated above, that argon and its companions are not absorbed by the calcium. It follows that if air is admitted to heated calcium the argon is left behind in a state of great purity. In the course of his investigations he constructed a vacuum tube and calcium apparatus of known volume, and admitted successively known amounts of air, the oxygen and nitrogen being absorbed between each admission with the result that a definite and known amount of argon accumulated in the apparatus. In one experiment the volume of the apparatus was 123 c.c.,

[1] For permission to reproduce this illustration I am indebted to Messrs. Plowden & Thompson, Ltd., Stourbridge, England.

[2] *Proc. Roy. Soc.*, **78**, 429 (1907).

and it was possible to admit a measured amount of 0·13 c.c. at one time. This quantity of air therefore corresponded to a pressure of argon of 0·0075 mm. It was found that after absorption of the oxygen and nitrogen no discharge would pass through the vacuum tube until three quantities of air had been admitted and absorbed. In other words a discharge would only just pass through argon under a pressure of 0·0225 mm. In the second experiment the volume of the apparatus was 100 c.c. and 12 c.c. of air were admitted after the calcium had been heated to the absorbing temperature. This quantity was absorbed without difficulty, and the residual argon must have exerted about 1 mm. pressure, yet the tube showed brilliant green phosphorescence.

It follows from these experiments that below a pressure of one-fiftieth of a millimetre, no discharge can be sent through a tube containing argon. At 0·5 mm. the resistance of the tube is greater than that of an air gap 5 mm. long, while at a pressure of 1 mm. the tube is brightly phosphorescent. It is evident from this that the generally accepted idea of high vacua must be modified, for it is usually assumed that when the electric discharge will not pass through a vacuum tube the pressure inside is vanishingly small; owing to the fact that monatomic gases such as argon, etc., refuse to allow the discharge to pass at so high a pressure as one-fiftieth of a millimetre, the non-conductance of a vacuum tube cannot be accepted as a criterion of the smallness of the gaseous pressure therein.

Soddy concludes from his results that the well-known fact that a vacuum tube filled with one of the rare gases becomes non-conducting after continued use is due to the absorption by the electrodes, not of the rare gas, but of the small traces of diatomic gas present, with the result that the former becomes perfectly pure and offers an abnormal resistance to the electric discharge. This explanation is, however, not necessarily correct. As has already been pointed out, when vacuum tubes with metallic electrodes are used with any one of the rare gases, the electrodes are disintegrated on the surface by the action of the discharge and a considerable amount of electrode "splash" is deposited on the walls of the tube. This splash tends to occlude the rare gases very effectively, even to their complete disappearance from the gaseous phase. If the glass walls which are covered with this splash are powdered and heated strongly a considerable proportion of the occluded gas can be recovered.[1]

The condensation or occlusion of gases by charcoal at the temperature of liquid air was first applied by Dewar.[2] The absorption of diatomic and polyatomic gases takes place with extreme readiness, and the vapour pressure of the gases thus condensed is extraordinarily small, so that this method may be used for a rapid and effective exhaustion of any apparatus, such as vacuum tubes. The best charcoal

[1] Baly and Riding, *Proc. Roy. Soc.*, A, **109**, 186 (1925).
[2] *Ibid.*, **74**, 122 (1904).

for the purpose is that made from cocoa-nut shells, and these may be charred in the following way. They are first broken into small pieces, which are put into a crucible and covered with silver sand. The crucible is heated in a furnace until no further distillation products are evolved. The crucible is then taken out of the furnace and allowed to get quite cold before the charcoal is taken out of the sand. The charcoal thus produced is then placed in a glass tube, which is sealed to the apparatus to be exhausted. This tube is then immersed in liquid air, and it will be found that the gases are rapidly absorbed with the production of a very high vacuum. It will be found advisable between each experiment to drive off all the gases condensed in the pores of the charcoal if the maximum absorbing power is to be exerted. This is simply enough carried out by heating the tube containing the charcoal with a Bunsen burner, and exhausting it with some form of air-pump. In order to protect the charcoal from exposure to the atmosphere when not in use, it is advisable to fit a stopcock to the tube containing it, which may be closed when the tube is not in use.

It must be remembered that the amount of occlusion which takes place with the rare gases, helium, argon, etc., is extremely small, and consequently this method may be used to separate these gases from a mixture with other gases. As an illustration of this, the presence of neon in the atmosphere may be demonstrated by means of a small vacuum tube to which is attached a tube containing charcoal. After the charcoal has been heated in a vacuum to remove the condensed gases from its pores, and allowed once again to cool, air is admitted. The charcoal is then cooled in liquid air and on passing the discharge through the vacuum tube the characteristic fiery red glow of neon will be seen. If this does not appear at first, a further quantity of air may be admitted and allowed to condense on the charcoal.

As has already been explained the usual method of exciting the luminescence of the gases in vacuum tubes is the high potential discharge from an induction coil or transformer with or without a condenser. The discharge is thus intermittent, and to a certain extent alternating. If a unidirectional discharge is desired, it is necessary to dispense with the condenser and introduce a rectifier into the circuit. Alternatively, a system of batteries may be used, but in this case, unless some method is adopted of breaking the initial resistance offered by the gas to the passage of the discharge, a very large number of such batteries in series will be required. Many methods have been used at various times to overcome this difficulty, but perhaps the best and most convenient is the Wehnelt cathode, as described by Wiedemann and Wehnelt.[1] These authors pointed out that if a piece of platinum foil covered with calcium, strontium, or barium oxide be used for the cathode in a vacuum tube, and be heated to redness, a current of several amperes, at 110 to 220 volts, may readily be

[1] *Phys. Zeitschr.*, **6**, 690 (1905).

made to pass through the tube. The effectiveness of this cathode is due to the fact that when heated it emits a stream of electrons which ionise the gas in the vacuum tube and so renders it capable of conducting a current of relatively low potential. It was shown also that, under these circumstances, the anode melts and volatilises, and the vapour from it is brilliantly illuminated by the discharge.

This is a most convenient method of examining metallic spectra. Konen and Jungjohann [1] have devised a special form of vacuum tube for this particular purpose of direct-current discharge. It is shown in Fig. 57. The two bulbs at the bottom of the tube are three centi-

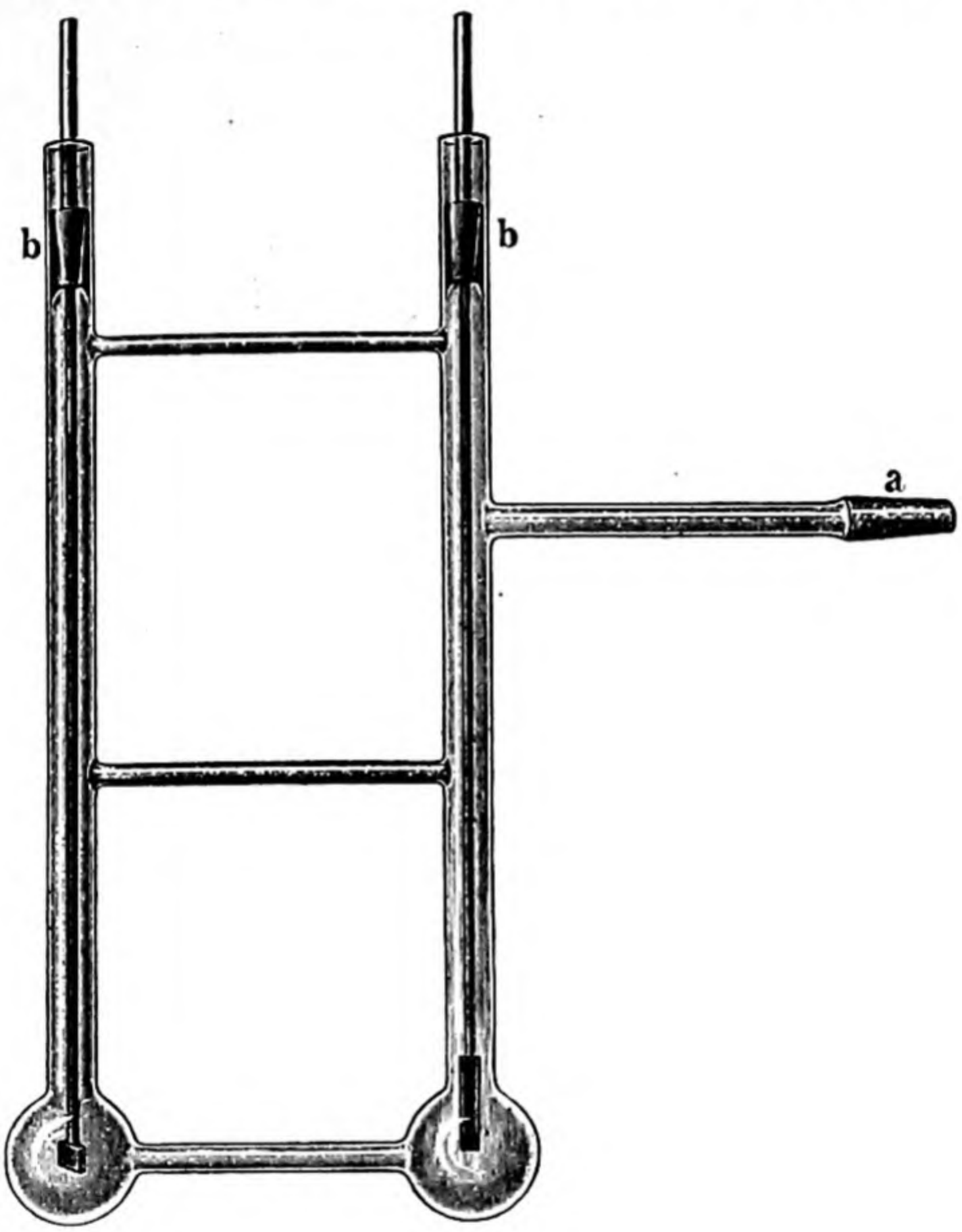


FIG. 57.

metres in diameter; the capillary tubing has a two-millimetre bore, and is about 66 mm. long. The electrodes are made of nickelled steel, and are ground in at *b*, *b*. It is advisable to cover this ground joint with a little mercury to guard against any leakage of air. The lower ends of these electrodes consist of aluminium cylinders, and the particular one to be used as cathode has a narrow slit cut in it, in which is fastened a small piece of platinum foil. This platinum is about 0·25 cm. square and 0·01 mm. thick, which has previously been dipped in an aqueous solution of barium and calcium nitrate, and then

[1] *Verh. d. Deutsch. Phys. Gesell.*, **12**, 145 (1910).

heated to redness in a Bunsen flame, so that it becomes covered with a thin layer of oxide. The authors, in using this tube, have employed a battery of 420 cells, which gives a potential difference of about 840 volts and a current of 1·2 amperes. It is not at all difficult to start the discharge passing in the tube, this being done simply by warming it with a Bunsen burner. The tube is most conveniently made of quartz, and may be joined to the glass apparatus necessary for exhaustion by means of the ground end at *a*.

Cathodoluminescence Spectra.—An interesting method of exciting the radiation of the spectra of metals by means of cathode rays has been developed.[1] This method was first realised by Hertz,[2] and later by Lewis,[3] who examined the spectra of several of the more volatile metals excited in this way. The later form of the apparatus used by Miss Carter and Dr. King is shown in Fig. 58, and consists of an inverted crucible-shaped vessel of silica which is ground to fit accurately on to a glass base-plate $\frac{3}{4}$-inch thick. Through the top of this vessel is bored a hole into which a silica tube T is fitted by tapering slightly at one end. Through this tube T passes a second silica tube, which is fitted into a hole bored into a silica crucible B, about 2 inches in diameter. The cathode C is made of copper, faced with iron, and is connected by a copper rod with the copper vessel E, into which ice is placed during the passage of the discharge. The object of the crucible B is to concentrate the discharge and protect the walls of the main vessel from blackening. All the joints are cemented with sealing wax. In the outer silica vessel two holes were drilled opposite to each other, and into these were fitted glass tubes carrying at their ends quartz windows for observation of the luminescence spectrum just above the anticathode.

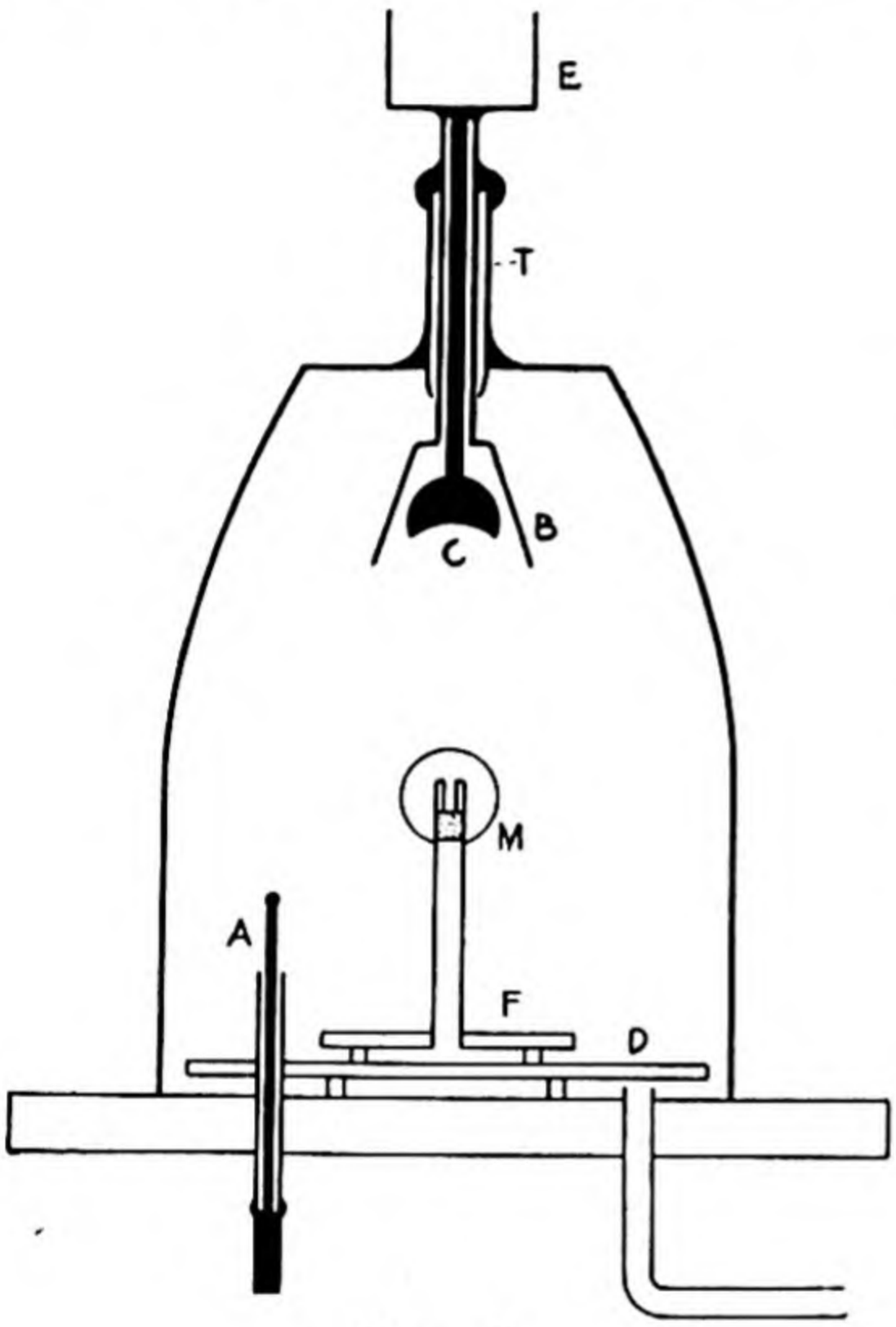


FIG. 58.

On the glass base-plate there rests an aluminium plate D which is $\frac{1}{4}$-inch thick, supported on feet, this being used to protect the glass from the heat. The anode A is introduced through a silica tube which is cemented into a hole drilled in the glass base-plate and passes

[1] A. S. King and Edna Carter, *Astrophys. Journ.*, **44**, 303 (1916); Edna Carter and A. S. King, *ibid.*, **49**, 224 (1919).

[2] *Wied. Ann.*, **19**, 809 (1883).

[3] *Astrophys. Journ.*, **16**, 31 (1902).

through the aluminium plate. The metal to be examined, M, is contained in a silica tube mounted on the silica base-plate F. This tube has two vertical slots cut in its upper end to expose the luminescent vapour and at the same time confine it, the metal being placed just below the bottom of the slot.

The apparatus is exhausted by two rotary oil-pumps placed in series and the discharge current is supplied by a transformer with a spark rectifier. As in Soddy's experiments with heated calcium, it is generally found that the effect of the discharge in vaporising the metal caused a rapid absorption of the residual gas. Sometimes this effect is sufficient to inhibit the discharge altogether, and it then becomes necessary to allow a very slow stream of air to leak in through a very fine capillary tube in order to maintain a sufficient quantity of gas for the discharge to pass.

The following metals were investigated with this apparatus: calcium, iron, manganese, titanium, magnesium, and cadmium. In the case of iron the anticathode was made the anode. It may be noted that some of the positive and negative bands of nitrogen were visible on the spectrum photographs.

Electrodeless Ring-Discharge.—A method of excitation of the vapours of the more volatile metals by means of the so-called ring-discharge has been described.[1] The inner coatings of three Leyden jars are connected with the two secondary terminals of a large 30-inch spark induction coil, whilst the outer coatings are earthed. The two sets of coatings are connected by a wire which forms a solenoid of two or three turns round the discharge apparatus, a zinc spark gap being introduced into this circuit. The induction-coil is supplied with direct current at 220 volts through a mechanical interrupter.

The discharge vessel may be a quartz bulb of 7 or 5 cm. diameter, the larger size being the better except for examination of the ultra-violet region. When a mercury pump is used to exhaust the discharge vessel it sometimes happens that the mercury spectrum is developed to an inconvenient extent, but it is stated that this can very largely be reduced by using a drying tube of phosphorus pentoxide. The spectra of zinc and cadmium in particular have been examined by this method. The metal is placed in the discharge tube and the latter, after exhaustion, is heated.

The cadmium spectrum, as obtained in this way, was measured between $\lambda = 6467{\cdot}4$ to $\lambda = 2183{\cdot}1$, and certain differences in the relative intensities of the lines as compared with those given by the arc and spark discharge were noted. All the arc lines with the exception of the weakest were present, and their relative intensities in general were found to be the same as in the case of the arc. There were noted, however, several exceptions, such as

[1] Hagenbach and Frey, *Phys. Zeitsch.*, **18,** 544 (1917); Hagenbach and Schumacher, *Zeitsch. wiss. Phot.*, **19,** 129, 142 (1919).

λ.	Arc.	Ring.
3729	4	1
3650	2	7

Both of these lines are absent in the spark spectrum.

As a general rule, those lines which exhibit different intensities in the arc and spark discharge appear in the ring discharge with the greater intensity. Thus

λ.	Arc.	Spark.	Ring.
5378	6	10	10
4663	8	3	10
3133	2	8	10
2775	6	4	7
2321	1	7	10

To this rule also were found some exceptions.

The enhanced lines which do not appear in the arc spectrum of cadmium exhibit remarkably different intensities in the ring discharge compared with those in the spark, some being more and others being less intense. As examples of this we have

λ.	Spark.	Ring.
4158	5	1
4142	4	5
3988	5	0

λ.	Spark.	Ring.
3984	3	1
3959	7	0
2948	4	0
2927	1	5

It is also of considerable interest to note the fact that 44 new lines of cadmium were observed in the spectrum of the ring discharge.

The spectrum of the ring discharge through zinc vapour was measured between $\lambda = 6362{\cdot}58$ and $\lambda = 2252{\cdot}87$. Here, again, new lines were observed to the number of 51. In general, the relative intensity of the arc lines given by the ring discharge was less than in the case of cadmium. Compared with the arc and spark spectrum of zinc the relative intensities of the lines in the ring discharge spectrum are very different.

It may further be noted that in the case of zinc a band spectrum was also observed and the wave-lengths of the component lines were measured. The bands extend from $\lambda = 4895$ to $\lambda = 3470$.

CHAPTER III.

THE NATURE OF SPECTRA.

Emission spectra may be divided into three classes, continuous spectra, band spectra, and line spectra. Continuous spectra are those which contain the whole group of wave-lengths between certain limits depending on various controlling influences. Such spectra are usually given by solid substances, the limits of continuous emission depending on the temperature. Emission band spectra can always be resolved into groups of very fine lines, each group having a "head." The lines of each group are so ordered that in one direction, either towards the longer or shorter wave-lengths, they get closer and closer together until they form a sharp edge or head. This head may be either on the red or ultra-violet side of the band, the band being degraded towards the ultra-violet or red. With low dispersion the appearance of these band spectra is that of a channelled or fluted spectrum, and these names are frequently met with in the literature.

Band spectra are always emitted by compounds and sometimes by elements, such for example as nitrogen when excited by the uncondensed discharge in vacuum tubes. Our knowledge of the emission spectra of compounds is less extensive than that of the elements, this being partly due to the fact that they are often unstable under the usual conditions of excitation. Although this knowledge has been advanced during recent years, yet Kayser's dictum still holds good: "Es liegt hier fruchtbares Arbeitsgebiet noch für Jahre und für zahlreiche Beobachter vor." [1]

As regards line spectra the position is very different, for of these our knowledge has during the last few years advanced by leaps and bounds as the result of the Bohr theory. In accordance with the scheme outlined at the beginning of the preceding chapter, this theory and the wonderful results it has brought in its train will be dealt with in Vol. III., Chapter I., its application to band spectra being discussed in Vol. III., Chapter IV.

There now await our consideration certain phenomena in connection with emission spectra, some knowledge of which is necessary for a full understanding of the present position as regards both line and band spectra. These subjects may well be grouped together in

[1] *Handbuch der Spectroscopie*, Vol. II., p. 222.

the present chapter, even though there will apparently be a certain amount of discontinuity. This cannot be helped at this stage, but their co-ordination will become obvious later. The first of these subjects is the characteristic properties of the individual lines in the line spectra of elementary atoms, and more particularly their structure and their breadth. Before discussion of the work which has been carried out in this direction, a few words may be said about the more general characteristics of emission lines. When the lines in the emission spectrum of an elementary atom are examined individually, they will as a rule be found to differ amongst themselves in their appearance. They are by no means all equally well defined, some of them are sharply defined on both sides, others are sharply defined on one side only, the other side being nebulous or diffuse, whilst others again are diffuse on both sides. Distinction may therefore be drawn between four different types of lines, namely (1) lines which are sharply defined on both sides, (2) lines which are sharp only on the side towards the longer wave-lengths, (3) lines which are sharp only on the side towards the shorter wave-lengths, (4) lines which are diffuse on both sides. This differentiation in type is of some importance, since lines which belong to the same spectral series are always of the same character. For example, as will be seen in Volume III., Chapter I., there exist a sharp series and a diffuse series in the spectra of many elements.

These differences in character of the lines of the spectrum of a substance are chiefly noticeable in the case of arc and spark spectra. In the spectra of gases in vacuum tubes the lines are almost always very narrow and sharply defined; this is no doubt due to the very low pressure that the gas is exerting. In certain cases, however, it is quite possible to meet with diffused lines in the spectrum of gases at low pressures. An interesting example of this is to be found with krypton and xenon;[1] when the oscillating discharge is passed through these gases, unless the pressure is below a certain small amount, the whole spectrum appears confused, and, indeed, almost continuous. If the pressure is then slowly reduced, the lines begin to appear upon a more or less continuous background, and, gradually increasing in brightness, they finally become quite sharply defined upon a black background. All the lines do not become equally well defined at once, some of the lines remaining more or less hazy until the pressure is reduced to a very low value. These results are very interesting, and not easy of explanation. The effect in certain cases of a small trace of impurity upon the lines of a spectrum is also very curious. It will very often be noticed that the presence of a small quantity of impurity masks the appearance of certain lines of a spectrum; for example, in the case of argon the admixture of a small quantity of impurity frequently masks the green lines given by this gas. This region appears confused, no definite lines being visible, while the red,

[1] Baly, *Phil. Trans.*, **202,** A, 183 (1903).

orange, and blue lines are quite distinct; the removal of the impurity brings out the green lines at once.

The Structure of Spectrum Lines.—The structure of spectrum lines was mentioned in the first chapter of this volume in connection with the application of interferential methods to spectroscopy, for it is only by means of these apparatus of great resolving power that investigations have been possible in this direction. Michelson (this Vol., p. 9) investigated a great number of lines with his interferometer, with the very important object of selecting an element which gives one or more lines sufficiently monochromatic to be used as standards of wave-length measurement. In view of the discussion in Chapter I. of the work carried out with interference apparatus, it is scarcely necessary to point out that the smaller is the divergence from the ideal of a true monochromatic radiation, the longer will be the difference in path possible with a given spectrum line. It is now a matter of history that Michelson found that the cadmium red line most nearly approaches the ideal monochromatic radiation of all the lines which he examined. For this reason of course this line has now been adopted as the fundamental standard of wave-length.

Michelson found that, with very rare exceptions, such as the cadmium red line, spectrum lines are complex. Each line is not a single entity with a measurable width, but is composed of a number of lines differing very slightly in wave-length from one another. Generally the structure consists of a limited number of principal components, together with a number of satellites. The results obtained by Michelson in this field are of considerable importance, in spite of the fact that more recent work has in some instances revealed still greater complexity than he was able to detect with his interferometer. The method employed by him, namely the analysis of the visibility curve, was explained in Chapter I., so that his results only need be quoted here.

Hydrogen.—With hydrogen at a pressure of about 1 mm., the red at line $\lambda = 6563$ is a double line, the two components of which have a ratio of brightness of 7 : 10; the distance between them is 0·14 A.U., and their half-width is 0·049 A.U. The blue line at $\lambda = 4860$ is again double, with the same ratio of brightness of the two components; the distance between them is 0·08, and their half-width 0·057.

Oxygen under reduced pressure.—The orange-red line $\lambda = 6158$ is a triple line; the components have their intensities in the ratio 1 : 1 : $\frac{1}{2}$, and their distances apart are 1·51 and 0·84 respectively, and their half-width is 0·027.

Sodium.—The results obtained from metallic sodium in the vacuum tube were so varied that a complete study was impossible. The following results were obtained under very low pressure and a temperature of 250° C. The D lines are both very close pairs, each pair being separated by about 0·02 A.U.; the intensities in each being about 10 : 8. Each of the components of the double yellow-green line at mean wave-length $\lambda = 5687$ is a single line. The

orange-red double at $\lambda = 6156$ seems to have a feeble component, and the doubles at $\lambda = 5150$ and 4982 are very similar.

Zinc.—Some observations were made on zinc vapour in vacuum tubes, but the necessary temperature melted the glass. The red line at about $\lambda = 6360$ is single, and has a half-width of 0·013. The blue line at about $\lambda = 4811$ has a small component nearly 0·2 A.U. distant.

Cadmium in a vacuum tube at a temperature of 280° gives a red line at $\lambda = 6439$, which is quite simple, with a half width of 0·0065. The green line $\lambda = 5086$ is a close double whose intensity ratio is 5 : 1 ; the distance between the components is 0·022, and their half-width 0·0048. The blue line at $\lambda = 4800$ is similar.

Thallium.—Thallium chloride was used in vacuum tubes. The green line gives a visibility curve, which can be explained by the line having two components, each of which is double.

Mercury.—The yellow line at $\lambda = 5790$ possesses a companion of feeble intensity at a distance of about 0·24 A.U. ; the line itself consists of a principal component with a faint double near to it. The intensities appear to be about in the ratio 10 : 2 : 1 ; and the distances 0·12 and 0·012 A.U. respectively. The yellow line at $\lambda = 5770$ appears to be a double, the components of which have the ratio of intensities 3 : 1 and are 0·019 A.U. apart. The green mercury line $\lambda = 5461$ is most complex ; the constituent lines are so fine that Michelson was able to extend his visibility curve to 400 mm. difference of path. The curve showed that the line is at least quadruple, with one bright component and three weaker ones. The violet line at $\lambda = 4358$ appears to have a faint component at a distance of 0·16 A.U.

It must be remembered that these values of Michelson's were obtained from his visibility curves ; when one of these was obtained for a particular source an equation was found which as nearly as possible expressed the results, and from this the distribution of intensity in the source was calculated.

The problem was subsequently investigated by Fabry and Perot with the help of their interferometer, and it may be pointed out that they were able actually to see the lines resolved and to measure the distances between the components, but not their breadths. Their results were not identical with those obtained by Michelson, but they give on calculation visibility curves which agree with those obtained by Michelson. In view of the fact that Fabry and Perot's observations do not possess the same inherent accuracy as the more recent measurements they need not be quoted here, with the exception of the green line of thallium at $\lambda = 5439$. This line was found to be triple, having two compounds of equal intensity on the red side, with distances from the principal component of 0·02 and 0·12 Ångströms, respectively.

More recent work has proved that the complexity of lines is in general far more complex than was evidenced by the researches of Michelson and of Fabry and Perot. A number of investigations have

been carried out in this field, amongst which may be mentioned those by Gehrcke and von Baeyer,[1] von Baeyer,[2] Janicki,[3] Galitzin,[4] Stansfield,[5] Gmelin,[6] Gale and Lemon,[7] Lunelund,[8] Stansfield and Walmsley,[9] Takamine,[10] Wali-Mohammad,[11] and Aronberg.[12] Very interesting and important work in this field has been carried out by Nagaoka,[13] and the results obtained by him may be given here. These measurements are worthy of note, since they reveal the existence of regularities in the distribution of the satellites.

In this type of work very high resolving power is necessary, such as is given by an echelon grating or a Lummer and Gehrcke interference plate. The advantage of crossing two of these plates was pointed out by Lummer and Gehrcke, who used the interference points thus obtained in their work on the lines of mercury. Nagaoka expressed the following views in his paper written in 1916.[14] The echelon grating and Lummer-Gehrcke plate have definite resolving power for a given wave-length, so that we cannot bring different powers to bear upon the lines to be analysed. The inconvenience is especially felt when the interval between successive spectra is so narrow that the lines are superposed and cause great confusion in discriminating between them. The disadvantage arising from the definiteness of the resolving power cannot be remedied, so that it is generally expedient to resort to those interferometers in which the thickness of the air space contributing to interference can be easily changed to suit the purpose of the experiment. A simple device for changing the resolving power is a prime factor that makes the interferometer of Fabry and Perot or Michelson indispensable in researches relating to the minute structure of a spectrum line, especially when it consists of a cluster of lines within narrow limits. The easiest way of arriving at a desired resolving power would be to increase the air interspace between the plates in a Fabry and Perot interferometer, the thickness being of course within the limit of interference for the line to be examined. One serious objection to a thick interspace is the crowding of the lines as different interference fringes are intermixed with each other, and hence arises the trouble of discriminating between the different lines, especially when there are numerous satellites. In fact the appearance of

[1] *Ann. der Phys.*, **20**, 269 (1906).
[2] *Verh. deutsch. phys. Ges.*, **9**, 84 (1907).
[3] *Ann. der Phys.*, **19**, 36 (1906); **29**, 833 (1909); **33**, 438 (1910).
[4] *Bull. Acad. Sci.*, St. Petersburg, 1907, p. 159.
[5] *Nature*, **78**, 8 (1908).
[6] *Ann. der Phys.*, **33**, 17 (1910).
[7] *Astrophys. Journ.*, **31**, 78 (1910).
[8] *Ann. der Phys.*, **34**, 505 (1911).
[9] *Phil. Mag.*, **23**, 25 (1912).
[10] *Proc. Math.-Phys. Soc.*, Tokyo, **8**, February, 1915.
[11] *Astrophys. Journ.*, **39**, 189 (1914).
[12] *Ibid.*, **47**, 102 (1918).
[13] *Nature*, **77**, 581 (1908); *Proc. Math.-Phys. Soc.*, Tokyo, **5**, 2, 140 (1909); **8**, 214, 220, 229, 571 (1915); *Phys. Zeitschr.*, **10**, 609 (1909); *Proc. Phys. Soc.*, London, **29**, 91 (1917); Nagaoka and Takamine, *Proc. Phys. Soc.*, London, **25**, 1 (1912); *Proc. Math.-Phys. Soc.*, Tokyo, **7**, 2, 141 (1913); *Phil. Mag.*, **27**, 126 (1914); Nagaoka and Sugiura, *Astrophys. Journ.*, **53**, 339 (1921).
[14] *Proc. Phys. Soc.*, London, **29**, 92 (1917).

interference rings is extremely vague, when the interspace is several centimetres thick, so that it is almost impossible to tell even the position of the strong satellites. This difficulty can, however, be to a great extent overcome by the use of interference points, obtained by crossing the first interferometer with another instrument, which may have either fixed or adjustable resolving power. The advantage gained by crossing is especially great when there is ambiguity in the position of the satellites as observed with a single instrument, for it can easily be settled by examining the crossed spectra. With an adjustable interferometer we can change the air interspace in such a way that the satellites to be analysed are brought distinctly under observation, without being intermixed with other components.

Nagaoka used the combinations of the Fabry and Perot interferometer with the echelon grating, Lummer and Gehrcke plate, wedge plate, and a Fabry and Perot étalon. The last method of crossing was found to have the disadvantage of too great loss of light owing to the four half-silvered surfaces, so that most of Nagaoka's work was done with the other two combinations. For work with fixed resolving power he found that excellent results were given by the combination of an echelon grating or a Lummer and Gehrcke plate with a wedge plate. For the details of the method of interpreting the interference point patterns reference must be made to Nagaoka's paper.

We may now consider the experimental results obtained by Nagaoka with the lines of mercury, cadmium, and bismuth.

The mercury line at $\lambda = 5461$. The principal line is a triplet with a strong satellite on the positive and negative sides. Several photographs were taken with different values of the air space in the Fabry and Perot interferometers, and these all gave the following values for the distances between these fine lines, expressed in milli-Ångströms,

$$-19{\cdot}9 \quad -8{\cdot}4 \quad 0 \quad +8{\cdot}2 \quad +18{\cdot}4;$$

of the satellites the outermost one at -237 is the most conspicuous and this may be used as a reference line for comparing the results of other observers, as suggested by Stansfield. In Table XXVI. the

TABLE XXVI.

0	0	0	0	0	+ 0·793
136	133	134	134	135	+ 0·341
169	166	168	168	167	+ 0·234
188	191	188	188	190	+ 0·157
213	220	216	214	216·9	+ 0·066
—	—	—	227	228·4	+ 0·027
237 ?	242 ?	246 ?	236	236·8	0
—	—	—	245	245·0	− 0·029
—	—	—	254	255·2	− 0·062
319	318	320	320	322	− 0·285
362	364	365	364	365	− 0·431
448	450	452	450	451	− 0·717

values given are referred to this satellite, and not to the principal line, the position of which is very vague, owing to its multiple character. In the last column are given the difference in wave-numbers per centimetre referred to the central line.

Nagaoka points out that there exists a remarkable symmetry in the distribution of the satellites in different lines. The general arrangement of the components of the 5461 line are shown in the upper row of Fig. 59,[1] the lengths of the lines in the figure being proportional to the intensity of the components. The arrangement in groups as indicated in the four lower rows of Fig. 59 shows the symmetry.

The principal line forms a triplet with the components at — 0·062 and + 0·066. The satellite at — 0·029 forms another triplet with the components at — 0·285 and + 0·234, the separations being — 0·263 and + 0·256, which is nearly four times the separation of the principal

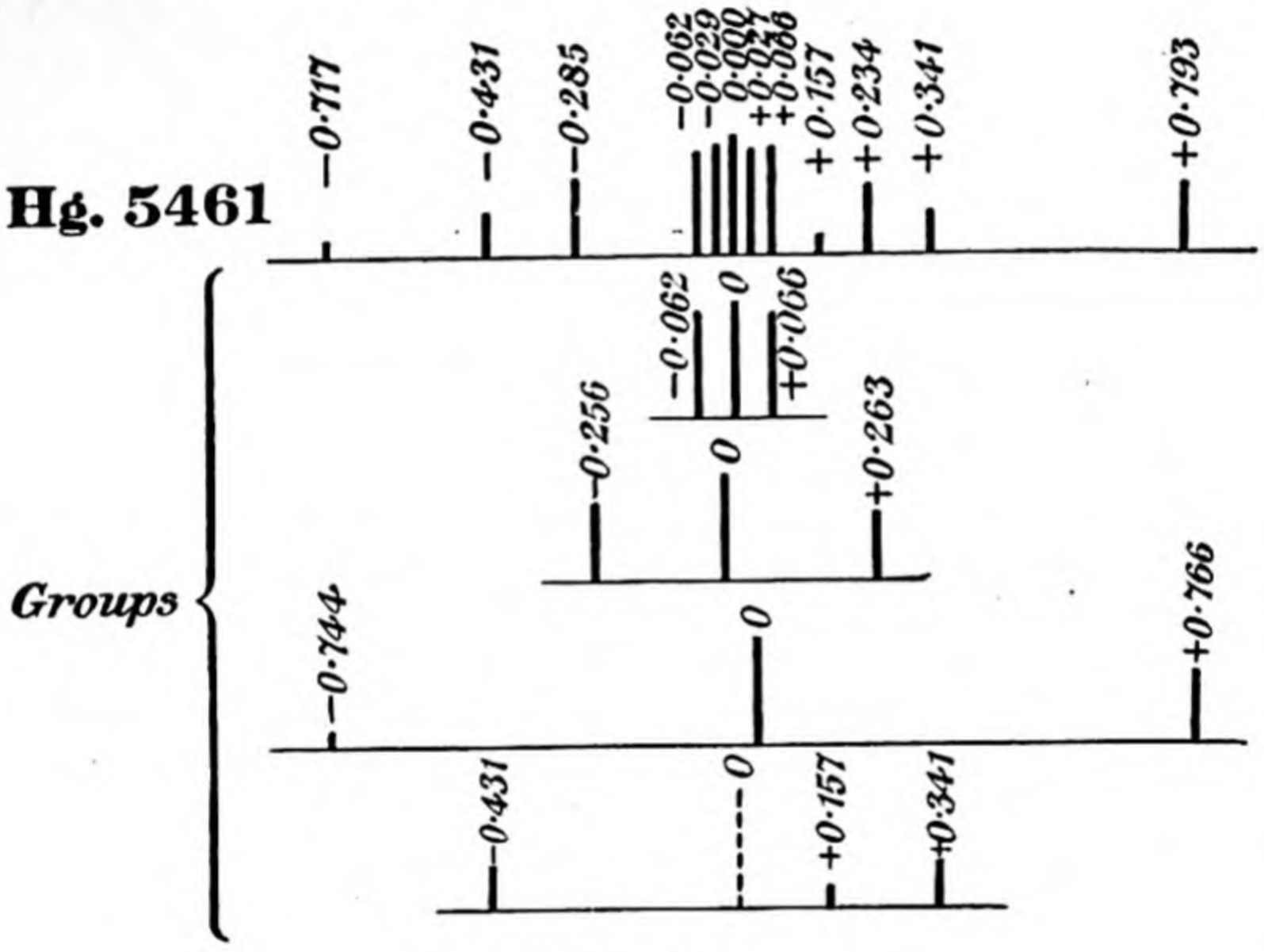


FIG. 59.

triplet. Then again, the component at + 0·027 forms a third triplet with the components at — 0·717 and + 0·793, the separations, — 0·744 and + 0·768, being about three times that of the second triplet and twelve times that of the first triplet. The remaining satellites at — 0·431, + 0·157, and + 0·341 have apparently no regularity. The first two triplets are also symmetrical as to their intensity distribution, but this is not the case with the third triplet. The wave-number intervals in the last row of Fig. 59 have a singular relation, since 0·431 — 0·157 = 0·274, 0·341 — 0·157 = 0·184, and 0·184 = 2/3 × 0·274.

In addition to this, we have the intervals between the satellites,

— 0·717 and + 0·341 = 1·058
— 0·285 and + 0·793 = 1·078

[1] This and the following four illustrations are reproduced by permission from the *Proceedings of the Physical Society*, Vol. 29. The Fleetway Press, London.

and the mean of these two is 1·068. This is not characteristic of the 5461 line only, since it will presently be seen that in the case of several mercury lines, the difference in wave-numbers of satellites is constant and about equal to the above number.

The mercury line $\lambda = 4359$. This line is more complex than the 5461 line, but the arrangement of the central components is somewhat similar, since the principal line forms a triplet, of which the middle component is somewhat weak compared with the side components, each of them being associated with a strong satellite. The separations of the components of this group again expressed in milli-Ångströms are :—

$$-17{\cdot}9 \quad -5{\cdot}8 \quad 0 \quad +5{\cdot}7 \quad +16{\cdot}2.$$

In Table XXVII. the separations are referred to the strong outermost satellite which is easily oriented.

TABLE XXVII.

von Baeyer.	Nagaoka and Takamine.		Nagaoka.	
—	—	—	− 78	+ 1·254
—	—	—	− 57	+ 1·082
0	0	0	0	+ 0·844
52	53	53	53	+ 0·566
66	67	66	65	+ 0·502
114	116	115	114	+ 0·245
142	142	140	139·8	+ 0·110
—	—	—	151·9	+ 0·047
159 ?	161 ?	163 ?	157·7	+ 0·015
—	—	—	163·4	− 0·015
178	181	180	179·6	− 0·099
187	193	189	190	− 0·154
203	206	206	207	− 0·244
273	267	268	268	− 0·566
—	—	—	318	− 0·834
344	344	345	343	− 0·956
—	—	—	383	− 1·176
—	—	—	398	− 1·251

The wave-number differences given in the last column are not calculated from what appeared to be the principal line, but the central point is laid at the mean position between the two strong components 157·7 and 163·4, so that these two form a strong doublet.

In Fig. 60 the components are plotted according to the wave-number differences in two rows, of which the upper shows remarkable symmetry. The lines in the lower row have no apparent symmetry, but the same type of regularity can be detected as in the case of the 5461 line. Thus the difference between the absolute wave-numbers 0·956 and 0·047 is 0·909, and that between 0·502 and 0·047 is 0·455, the ratio of the two differences being 2 : 1. Further, the wave-number

difference between the principal component — 0·015 and the satellite — 1·176 is 1·161, which is double the difference between the two positive satellites + 0·502 and 1·082.

As in the case of the green line there are the following constant wave-number differences between—

— 1·176	and	— 0·099	= 1·077
— 0·956	,,	+ 0·110	= 1·066
— 0·834	,,	+ 0·245	= 1·079
— 0·564	,,	+ 0·502	= 1·066
— 0·244	,,	+ 0·844	= 1·088
+ 0·015	,,	+ 1·082	= 1·067
		Mean	= 1·074

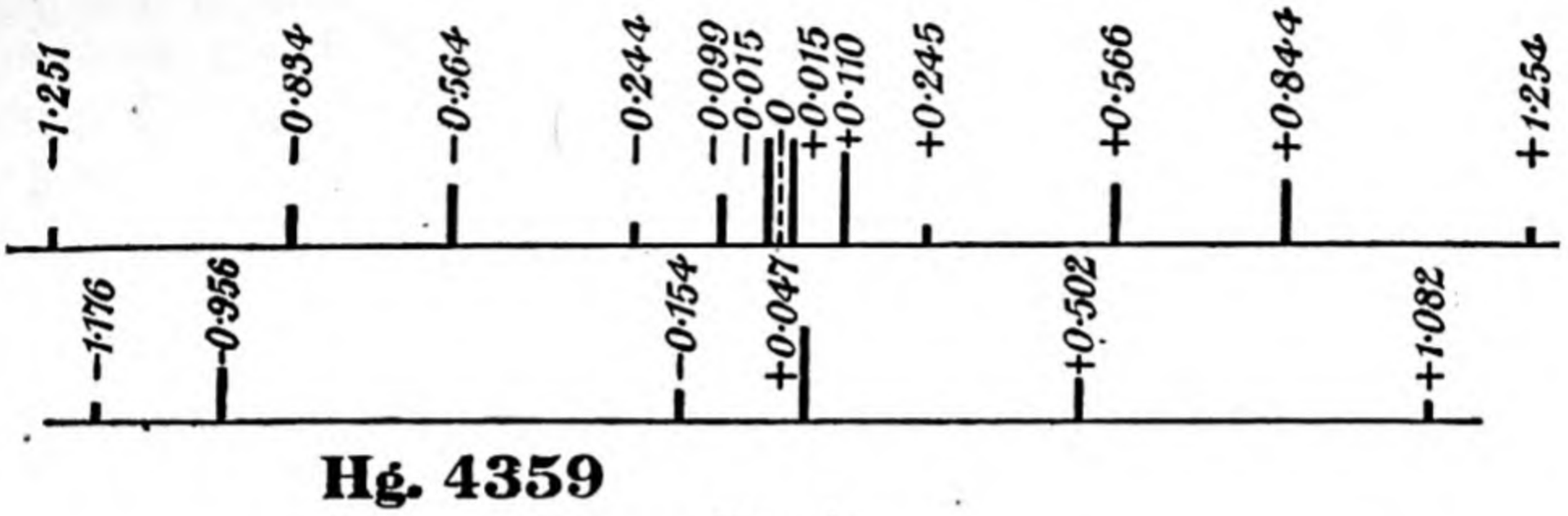


FIG. 60.

The corresponding interval in the green line has a mean value of 1·068, which is very near to the present value. Moreover, the interval between

— 1·251	and	— 0·244	= 1·007
+ 0·245	,,	+ 1·254	= 1·009
		Mean	= 1·008

The difference between the two intervals is 0·066, which is the interval between + 0·566 and + 0·502, and also corresponds to the wave-number difference found in the triplet of the 5461 line. These apparently are not chance coincidences, since they also occur in the line $\lambda = 4047$.

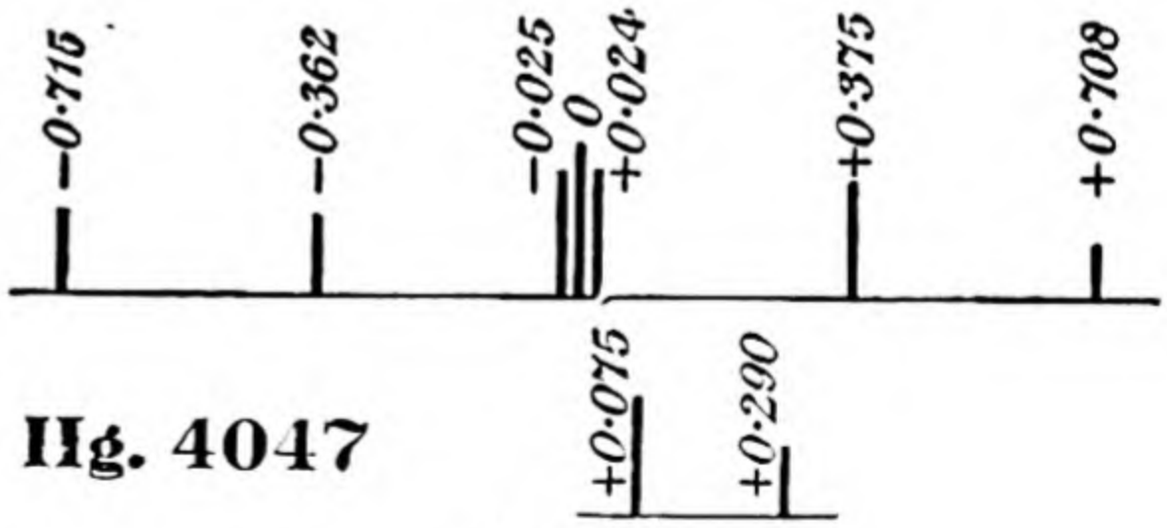


FIG. 61.

The mercury line $\lambda =$ 4047. This line consists of nine components, the principal line being a triplet accompanied by a satellite. The wave-number differences referred to the principal components are — 0·715, — 0·362, — 0·025, 0, + 0·024, + 0·075, + 0·290, + 0·375, + 0·708, and their distribution is diagrammatically shown in Fig. 61. The upper row shows the principal triplet and two satellites on each side symmetrically situated with

respect to it. The two satellites in the lower row are evidently not to be included in the scheme of symmetry.

In this case there are the wave-number intervals between

$$\begin{aligned} -0{\cdot}715 \text{ and } +0{\cdot}375 &= 1{\cdot}090 \\ -0{\cdot}362 \quad ,, \quad +0{\cdot}708 &= 1{\cdot}070 \\ \text{Mean} &= 1{\cdot}080 \end{aligned}$$

This value agrees with that previously found in the 5461 and 4359 lines. Moreover, the ratios between the mean interval 0·368 and 1·080 is 1 : 3, and that between the mean interval 0·712 and 1·080 is 2 : 3.

It is possible that the similarity in the distribution of the satellites and the wave-number intervals is due to the character of the sharp series to which the above three lines belong. If the wave-number intervals are arranged somewhat differently, it will be seen that many of them are common to two or all three of the above lines. In Table XXVIII. the wave-numbers are referred to the following components, $+0{\cdot}793$ for $\lambda = 5461$; $+0{\cdot}844$ for $\lambda = 4359$; and $+0{\cdot}708$ for $\lambda = 4047$.

TABLE XXVIII.

λ = 5461.	λ = 4359.	λ = 4047.	λ = 5461.	λ = 4359.	λ = 4047.
—	+ 0·410	—	− 0·766	—	—
—	+ 0·238	—	− 0·793	− 0·797	—
0	0	0	− 0·822	− 0·828	—
—	− 0·278	—	− 0·855	− 0·859	—
—	− 0·342	− 0·333	—	− 0·943	—
—	—	− 0·418	− 1·078	− 1·088	− 1·070
− 0·452	—	—	− 1·224	—	—
− 0·559	—	—	—	− 1·408	− 1·423
—	− 0·599	—	− 1·510	—	—
− 0·636	—	− 0·633	—	− 1·678	—
—	—	− 0·684	—	− 1·800	—
—	—	− 0·708	—	− 2·020	—
− 0·727	− 0·734	− 0·733	—	− 2·095	—

It is evident that the three lines are not independent of each other and that the satellites are not arbitrarily distributed. It is a question why the above coincidences are not found when the components are measured with reference to the principal line.

The mercury lines at $\lambda = 5769$ and 4078. Turning to lines of other series, we find that the line at $\lambda = 5769$ gives a triplet about the principal component with wave-number intervals $-0{\cdot}139$, 0, $+0{\cdot}147$, and a component at $+0{\cdot}360$. The line at $\lambda = 4078$ gives six components with wave-number intervals $-0{\cdot}429$, $-0{\cdot}283$, $-0{\cdot}183$, 0, $+0{\cdot}285$, $+0{\cdot}466$. It will be seen that certain similarities between the intervals are shown by these two lines. Thus the interval between the two components $-0{\cdot}283$ and $+0{\cdot}285$ of the second line is twice that between the two components $-0{\cdot}139$ and $+0{\cdot}147$ of the first

line. Again, the interval 0·360 shown by the first line is double the interval 0·183 of the second line. Further, the successive intervals between the three components of the 5769 line, — 0·139, + 0·147, and + 0·360 are 0·286 and 0·213, and these are in the ratio 4 : 3. Nagaoka remarks that each of these lines has other satellites which were difficult to observe.

The mercury lines at $\lambda = 3663$, 3655, and 3650. These lines belong to the diffuse series and were examined by Takamine,[1] their structure being shown in Fig. 62. Here again the same constant

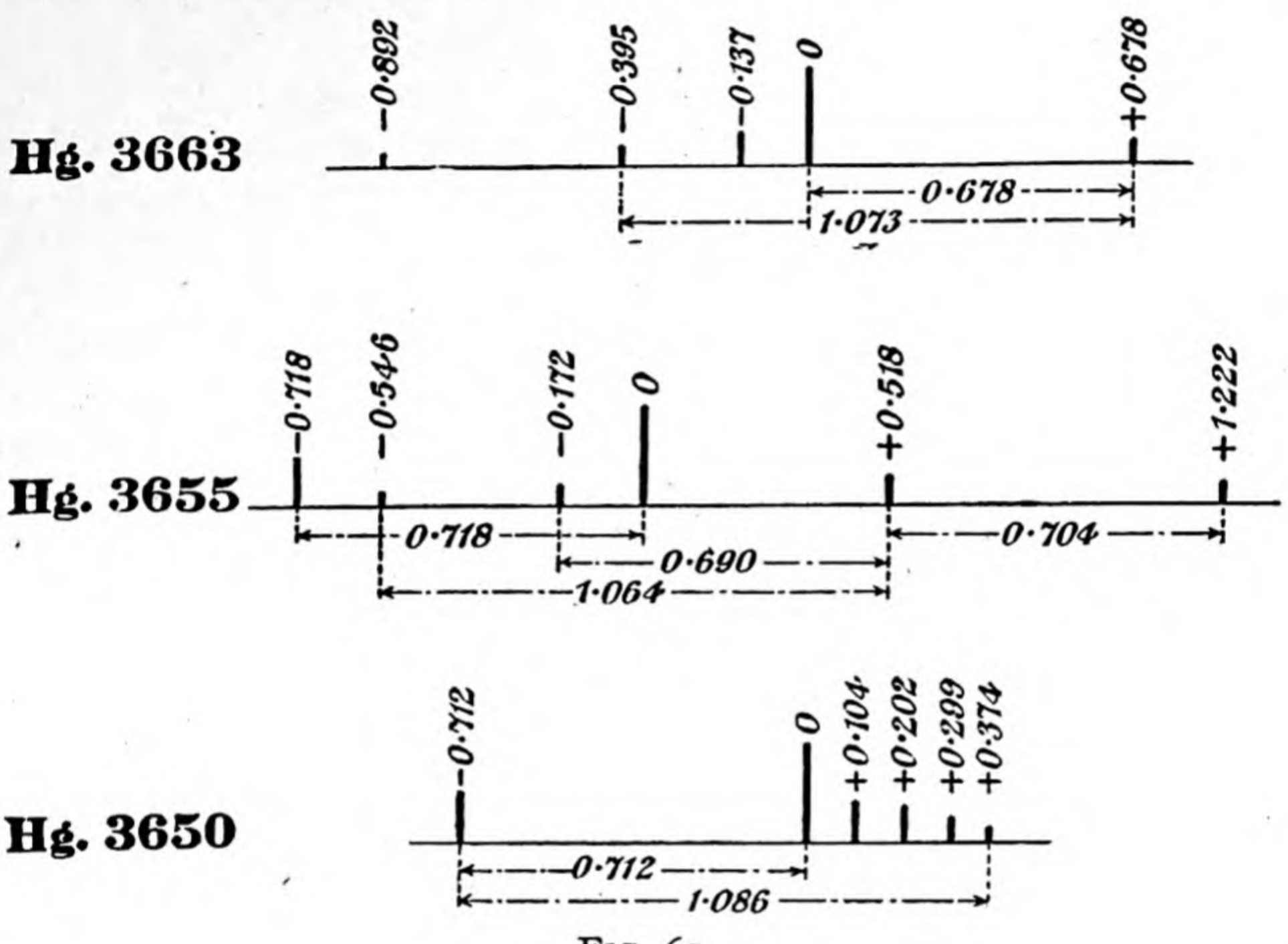


FIG. 62.

wave-number interval is found as in the lines of the sharp series, for they have the intervals between

$$\begin{aligned} -0{\cdot}678 \text{ and } +0{\cdot}395 &= 1{\cdot}073\ (\lambda = 3663) \\ -0{\cdot}546 \quad ,, \quad +0{\cdot}518 &= 1{\cdot}064\ (\lambda = 3655) \\ -0{\cdot}374 \quad ,, \quad +0{\cdot}712 &= 1{\cdot}086\ (\lambda = 3650) \end{aligned}$$

$$\text{Mean} = 1{\cdot}074$$

There is also a second constant interval between

$$\begin{aligned} -0{\cdot}678 \text{ and } \quad 0 \quad &= 0{\cdot}678\ (\lambda = 0663) \\ -0{\cdot}718 \quad ,, \quad 0 \quad &= 0{\cdot}718\ (\lambda = 3655) \\ -0{\cdot}172 \quad ,, \quad +0{\cdot}518 &= 0{\cdot}690\ (\lambda = 3655) \\ +0{\cdot}518 \quad ,, \quad +1{\cdot}222 &= 0{\cdot}704\ (\lambda = 3655) \\ -0{\cdot}712 \quad ,, \quad 0 \quad &= 0{\cdot}712\ (\lambda = 3650) \end{aligned}$$

$$\text{Mean} = 0{\cdot}700$$

[1] *Proc. Math.-Phys. Soc.*, Tokyo, **8**, 309 (1915).

and these two intervals, 1·074 and 0·700, are nearly in the ratio 3 : 2. The interval 0·711 occurs also in the 4047 line. It is of some interest to note that the intervals given by $0{\cdot}71 \times l/3$, $0{\cdot}71 \times m/4$, and $0{\cdot}71 \times n/5$, where $l = 1, 2, 3, 4$; $m = 1, 2, 3, 4, 5, 6, 7$; $n = 1, 2, 3, 4, 5, 6, 7$, are found amongst the components of the above eight mercury lines.

The three cadmium lines at $\lambda = 5086$, 4820, and 4678 were also examined by Takamine,[1] and Nagaoka shows that regularities also exist in their structure. This structure is simpler than in the case of the mercury lines and is shown in Fig. 63. In the first place there is a constant wave-number interval between

− 0·297 and + 0·097 = 0·394 (λ = 5086)
− 0·256 ,, + 0·143 = 0·399 (λ = 4800)
− 0·144 ,, + 0·260 = 0·404 (λ = 4678)

Mean = 0·399

This interval evidently corresponds to those found for the mercury lines, namely 1·07 and 0·71. Then again, in the 5086 line the separation of the negative component is very nearly three times that of the positive component. Further, in the 4800 line the interval 0·399 is very nearly twice the interval 0·204. Lastly, the distribution of the two satellites of the 4678 line is the reverse of that of the negative and first positive satellites of the 4800 line.

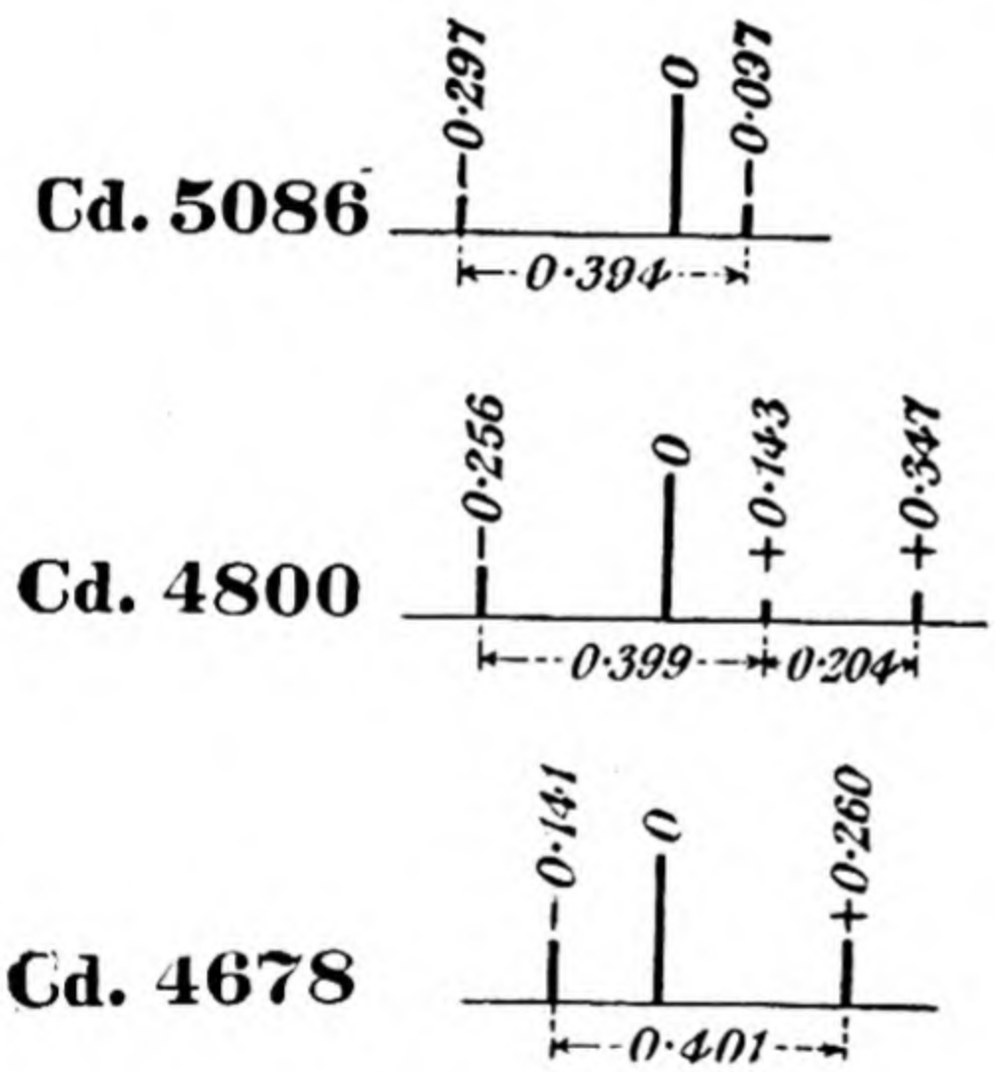


FIG. 63.

Equally interesting results were obtained in the case of three bismuth lines, which were examined by Nagaoka and Sugiura.[2]

The bismuth line at $\lambda = 4722$. This line possesses thirteen or fourteen components, the separation of which in Ångströms is given in Table XXIX., together with those of some previous observers.

The bismuth line at $\lambda = 4308$. Although the complete details of this line were not clearly made out from the photographs, there is no doubt that it consists of two doublets with two faint satellites as shown in Fig. 64.

The bismuth line at $\lambda = 4122$. Four components of this line were observed with the following separations in Ångströms :—

+ 0·122, 0, − 0·200, − 0·321,

[1] *Proc. Math.-Phys. Soc.*, Tokyo, **8**, 51 (1915).
[2] *Astrophys. Journ.*, **53**, 345 (1921).

TABLE XXIX.

Gehrcke and von Baeyer.	Takamine.	Aronberg	Nagaoka and Sugiura.	Int.
+ 0·316A	+ 0·320A	+ 0·318A	+ 0·317A	7
+ 0·289	+ 0·284	+ 0·284	+ 0·284	7
+ 0·242	+ 0·238	+ 0·240	+ 0·243	8
—	—	—	+ 0·179 ?	1
+ 0·104	+ 0·102	+ 0·102	+ 0·102	6
+ 0·057	+ 0·056	+ 0·056	+ 0·057	8
0	0	0	0	10
—	—	—	− 0·032	1
—	—	—	− 0·072	1
—	—	—	− 0·124	0·5
—	—	—	− 0·165	0·5
—	—	—	− 0·218	3
—	—	—	− 0·279	1
—	—	—	− 0·328	1

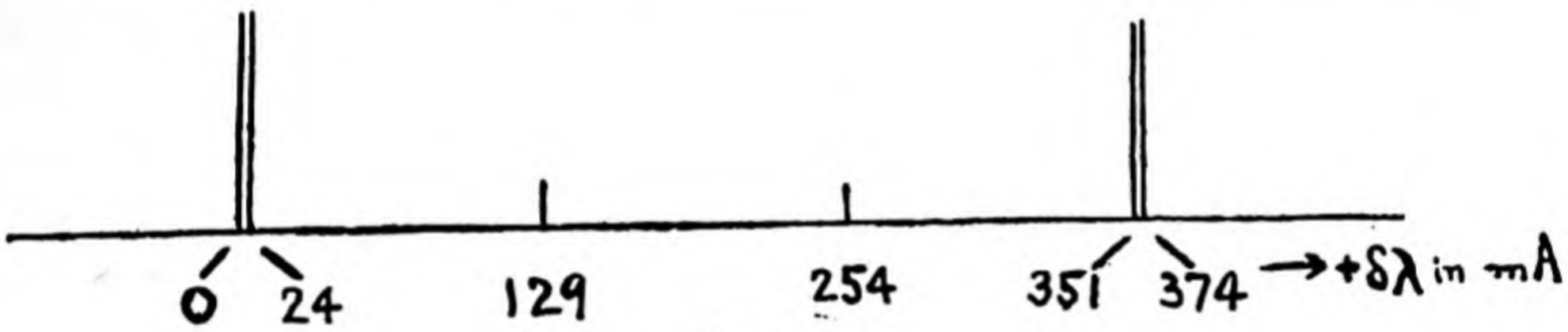


FIG. 64.

the two middle components having the greatest intensity. In order to investigate the regularities in the distribution of the components of these three bismuth lines the values given above must be reduced to wave-numbers, and these are set forth in Table XXX.

TABLE XXX.

Δν.	Δν.	Δν.
A. λ = 4772 − 142·2	B. λ = 4308 − 63·1	C. λ = 4122 − 71·8
− 127·3	+ 57·1	+ 117·6
− 80·3	12·7	+ 188·5
− 45·8		
− 25·6		
0		
+ 14·4		
+ 32·3		
+ 55·6		
+ 74·0		
+ 97·8		
+ 125·0		
+ 147·0		

From these we find :—

C 117·6 − 0 = 117·6
188·5 − 71·8 = 116·7
B 63·1 + 57·1 = 120·2
A 142·2 − 25·6 = 116·6
A 147·0 − 32·3 = 114·7

Mean = 117·1 = D_1

C 71·8 − 0 = 71·8
B 63·1 + 12·7 = 75·8
A 147·0 − 74·0 = 73·0
A 125·0 − 55·6 = 69·4
A 74·0 − 0 = 74·0
A 45·8 + 25·6 = 71·4

Mean = 72·6 = D_2

C 117·6 − 71·8 = 45·8
B 57·1 − 12·7 = 44·4
A 45·8 − 0 = 45·8
A 127·3 − 80·3 = 47·0
A 97·8 − 55·6 = 42·2

Mean = 45·0 = D_3

A 147·0 = 2 × 73·5
A 142·2 = 2 × 71·1

Mean = 2 × 72·3 = 2 × D_2

A 127·3 = 2 × 63·6
A 125·0 = 2 × 62·5

Mean = 2 × 63·1 B

A 25·6 = 2 × 12·8 B
B 188·5 = 3 × 62·8 B
A 127·3 = 3 × 42·4 = 3D_3
C 71·8 = 5 × 14·4 A
B 63·1 = 5 × 12·6 B

In addition to these relations it may be noted that the three constant differences D_1, D_2, D_3 are approximately in the ratio 5 : 3 : 2.

Nagaoka found that in the case of the bismuth line $\lambda = 4722$ the intensity was inclined to fluctuate. At first he believed that the whole line was subject to alternations of intensity, but observation showed that only a small portion of the line was subject to flickering, from which it appeared that what was supposed to be a single line consists of three or four lines closely packed together as is the case with the mercury 5461 line. It is strange that all parts of the line are not simultaneously affected. This observation agrees with those made by Exner and Haschek,[1] who investigated the structure and distribution of intensity in certain lines in the spectra of a number of elements. They claimed to have found undoubted evidence of the variation both in the number and in the relative intensity of the principal line and the satellites, and also in the relative intensity of the satellites amongst themselves. These variations are produced by slight alterations in the current and the density of the vapour of the element in question. The result of these variations is that with a spectroscope of small revolving power, such as a grating, the position of the whole line appears to shift.

The Breadth of Spectrum Lines.—It has been long known that the width of the spectrum lines of a substance increases when the pressure is increased ; this was first noticed by Ångström [2] in 1853 in the case of hydrogen, and further examined by many other observers, among the earliest of whom may be mentioned Wüllner,[3] and Lockyer

[1] *Wiener Ber.*, **116**, 2*a*, 323 (1907).
[2] *Pogg. Ann.*, **94**, 141 (1855).
[3] *Ibid.*, **137**, 339 (1869).

and Frankland.[1] That the lines do not, however, become infinitely narrow as the pressure falls to zero has been shown by Michelson, who has carried out by means of his interferometer very valuable quantitative work upon this subject. In Chapter I. was given an account of Michelson's method of determining the visibility curves of the lines from which he calculates the "half-width." If the intensity distribution of a line of finite width is plotted on a curve of which the abscissæ x are oscillation frequencies and the ordinates some function of x, then Michelson defines the half-width of the line to be the value of x when the function of $x = \frac{1}{2}$. Michelson found that the distribution of intensity cannot be very far different from that required by Maxwell's law, namely, that—

$$\phi(x) = e^{-p\frac{x^2}{a^2}}$$

where e is the base of natural logarithms and p and a are constants.

In 1889 Lord Rayleigh[2] showed from the standpoint of the kinetic theory that the motion of the molecule in the line of sight can produce a broadening of the lines of a spectrum. Several other explanations of the finite breadth of a line have been advanced, but Michelson has shown that at all events the Doppler principle[3] is the principal cause at work when the density is low, thereby neglecting the effect of collisions. In a first paper[4] Michelson, starting from Rayleigh's equation, arrives at the expression—

$$\Delta = \frac{1}{\pi}\sqrt{\frac{\log_e 2}{\pi}} \cdot \frac{V}{v},$$

where Δ is the difference in path (between the two interfering light beams in his apparatus) when the visibility has fallen to half the value it had at the centre of the line, V is the velocity of light, v is the velocity of translation of the molecules of the substance, and λ is the wave-length. From this we have, approximately—

$$\frac{\Delta}{\lambda} = 0{\cdot}15\,\frac{V}{v}.$$

If we take for hydrogen $v = 2000$ metres per second, then—

$$\frac{\Delta}{\lambda} = 22500.$$

Again, if we ignore the difference of temperature between the various substances examined, the velocity v will vary inversely as the square root of the atomic weight, and the number of waves $\left(\frac{\Delta}{\lambda}\right)$ in the difference of path at which the visibility is $\frac{1}{2}$ will be $22500\sqrt{m}$, where m is

[1] *Proc. Roy. Soc.*, **17**, 288 (1869); see Schuster, *Brit. Ass. Report* (1880), 277.
[2] *Phil. Mag.*, **27**, 298 (1889).
[3] For an account of the theory of the Doppler principle, see Vol. IV.
[4] *Phil. Mag.*, **34**, 280 (1892).

the atomic weight. Michelson tabulates the results he obtained on the structure of the lines giving the values of $\frac{\Delta}{\lambda}$, both found by experiment and calculated from the formula, and these are given in Table XXXI.

TABLE XXXI.

Substance.	A.W.	λ.	Δ.	$\frac{\Delta}{\lambda}$.	$\frac{\Delta}{\lambda}$ calculated.
Hydrogen . .	1·0	656	19·0	30000	22500
,, . .	1·0	486	8·5	18000	22500
Oxygen . .	16·0	616	34·0	55000	80000
Sodium . .	23·0	616	66·0	107000	108000
,, . .	23·0	589	80·0	133000	108000
,, . .	23·0	567	62·0	109000	108000
,, . .	23·0	515	44·0	85000	108000
,, . .	23·0	498	55·0	110000	108000
Zinc . . .	65·5	636	66·0	104000	182000
,, . . .	65·5	481	47·0	98000	182000
Cadmium . .	112·0	644	138·0	215000	238000
,, . .	112·0	509	120·0	236000	238000
,, . .	112·0	480	64·0	134000	238000
Mercury . .	200·0	579	230·0	400000	317000
,, . .	200·0	577	154·0	270000	317000
,, . .	200·0	546	230·0	420000	317000
,, . .	200·0	436	100·0	230000	317000
Thallium . .	203·6	535	220·0	400000	322000

In a later paper [1] Michelson gives some further results, in which he includes the substances just given, but he expresses the values as molecular velocities; in Table XXXII. v_1 are those calculated from the square root of the atomic weight, and v_2 those found from the observations $\left(v = \frac{0{\cdot}15V \times \lambda}{\Delta}\right)$.

It must be remembered that no allowance is made for temperature in these tables, because of the great uncertainty about its magnitude; under these conditions the agreement between theory and fact is very striking.

In order to show conclusively that the effect of density can be neglected in the above results, Michelson determined the amount of broadening of the lines of hydrogen caused by increasing the pressure, thereby increasing the number of molecular collisions. These collisions tend to limit the number of regular vibrations on account of the more or less abrupt changes of phase, amplitude, or plane of vibration produced, thus causing a widening of the line. The "half-breadths" of the hydrogen red line at different pressures are given in Table XXXIII.

[1] *Astrophys. Journ.*, **3**, 251 (1896).

TABLE XXXII.

Substance.	A.W.	v_1.	v_2.
Hydrogen	1	2000	1500
Lithium	7	800	1200
Oxygen	16	500	800
Sodium	23	400	400
Magnesium	24	400	650
Iron	56	260	500
Cobalt	59	260	560
Nickel	59	260	500
Copper	63	250	450
Zinc	65	250	450
Palladium	106	190	250
Silver	108	190	250
Cadmium	112	190	220
Gold	196	140	225
Mercury	200	140	140
Thallium	204	140	110
Bismuth	210	140	150

TABLE XXXIII.

Pressure in mm.	Half-breadth in A.U.
90·0	0·128
71·0	0·116
47·0	0·095
23·0	0·071
13·0	0·056
9·0	0·053
3·0	0·050
0·5	0·048

These results show that below a pressure of 5 mm. the effect of the collisions has almost entirely ceased, so that with decreasing pressure a limiting breadth of the hydrogen red line (and others too) is reached, and this limiting breadth is due to the Doppler effect; that is to say, it depends upon the substance itself and upon the temperature.

Michelson deduces an expression for the breadth of spectrum lines on the assumption that this is the sum of the separate widths due (1) to the motion in the line of sight, (2) to the limitation of the free path of the molecules. We have then $b = \delta_1 + \delta_2$, where δ_1 and δ_2 are the widths due to (1) and (2) respectively.

First the motion in the line of sight. Rayleigh's formula, as modified by the definition of visibility, becomes—

$$\text{Visibility} = e^{-\pi\left(\frac{\pi X}{\lambda}\cdot\frac{v}{V}\right)^2},$$

where X is the difference of path in the interferometer, *i.e.* the abscissa on the visibility curve, and v and V are the velocities of translation of the molecules and of light respectively. If, again, Δ, as before, is the value of X, for which the visibility becomes half the value it had when $x = 0$,

then
$$\Delta = \frac{1}{\pi}\sqrt{\frac{\log_e 2}{\pi}} \cdot \frac{V}{v}\lambda.$$

Now, as was shown on p. 8, the half-breadth of a line measured in oscillation frequencies was equal to $\frac{\log_e 2}{\pi\Delta}$, or in wave-lengths to $\frac{\log_e 2}{\pi\Delta}\lambda^2$, so that for the practical complete breadth of the line we have—

$$\delta_1 = \frac{2\log_e 2}{\pi\Delta}\lambda^2.$$

On substituting the above value of Δ,

then
$$\delta_1 = 2\sqrt{\pi \log_e 2} \cdot \frac{V}{v}\lambda$$
$$= 3\frac{v}{V}\lambda \text{ very nearly.}$$

For the second source of width of the lines Michelson deduces the expression—

$$\delta_2 = \frac{\lambda^2}{\rho} \cdot \frac{v}{V},$$

where ρ is the free path of the molecule.

From these two values for δ_1 and δ_2 we have—

$$b = \frac{v}{V}\lambda\left(3 + \frac{\lambda}{\rho}\right).$$

To find the effect of temperature and pressure changes according to this formula, we may put v = the molecular velocity at absolute temperature θ, and v_0 = the corresponding velocity at θ_0 (0° C.), m = the molecular weight, d = the actual density, and d_0 the standard density at θ_0, and ρ the length of free path at d_0; we then have—

$$b = \frac{v_0}{V} \cdot \frac{\lambda}{\sqrt{m}} \cdot \frac{\sqrt{\theta}}{\sqrt{\theta_0}}\left(3 + \frac{\lambda}{\rho} \cdot \frac{d}{d_0}\right).$$

In view of the imperfect assumptions made it will be better not to attach too much weight to the value of the constants, but we may examine the general formula—

$$b = \sqrt{\frac{\theta}{m}} \cdot \lambda(a + b\lambda d).$$

Michelson experimentally verified this formula to a certain extent, and found that it may be considered as a very good first approximation to the truth. The following points seemed to be well established :—

1. When the pressure is below one-thousandth of an atmosphere, the second term, $b\lambda d$, may be neglected.

2. Under this condition the width of the line is inversely proportional to the square root of the molecular weight.

3. The width increases as the temperature rises, the rate being not very different from that of the square root.

4. When the pressure is increased, the width increases in a nearly linear proportion.

5. The rate of this increase varies considerably with different substances, but in general it is more rapid the smaller the molecular weight, and while the general results can scarcely be said to prove that the rate is inversely as the square root of the molecular weight, they do not differ much from this proportionality.

6. At low pressures the proportionality with λ is not proved, there being about as much evidence for an increase of δ with λ as for a decrease.

7. At high pressures the width increases with wave-length, but the exact law was not determined.

8. The nature of the surrounding gas or vapour is of secondary importance.

Michelson deals further with the possible broadening due to the direct modification of the period of the vibrating atoms in consequence of the presence of neighbouring molecules. He points out that at pressures below one atmosphere the length of the free path is of the order of one hundred times the radius of the sphere of action of the molecules. It therefore appears that the number of free vibrations is also at least one hundred times as many as those whose period is modified by collision, and the effect of these modified vibrations would be correspondingly small in broadening the spectral lines except at great densities ; at these greater densities it seems not unlikely that the mutual influence of the molecules may be of great importance.

Again, where the broadening of the line is unsymmetrical, Michelson shows that such broadening can be explained by certain assumptions concerning the law of action of the molecules on their rates and intensities of vibration. All such lines should, starting from zero pressure, broaden symmetrically at first, and the asymmetrical broadening should not appear until the pressure is very considerable.

In a later paper,[1] Lord Rayleigh developed the formula—

$$\frac{\delta\lambda}{\lambda} = 3{\cdot}57 \times 10^{-7}\sqrt{\frac{\overline{T}}{m}}$$

[1] *Phil. Mag.*, **29**, 274 (1915).

where $\delta\lambda$ is the half-width of the line, T the absolute temperature and m the mass of the radiating particle. The application of this to the determination of the mass will be discussed below in connection with the secondary spectrum of hydrogen.[1]

The Length of Spectrum Lines.—There will be found, more particularly in the earlier literature of spectroscopy, frequent references to long and short lines in arc and spark spectra. Owing to the more scientific classification of lines in series and also on a temperature scale such as has been done by King, these terms are far less frequently used at the present time. In order, however, that the origin of the terms may be understood, a few words may be said about them. When an arc or spark is examined it will be found that all the spectrum lines do not reach right across the discharge from one electrode to the other. Such lines were called short lines in contradistinction to the long lines which traverse the whole distance. This classification of lines according to their length is of some interest because it marked the first attempt to recognise differences between the lines of a given spectrum. Amongst the earlier work may be mentioned that of Lockyer and Frankland [2] in 1869, who concluded that the length of a line would give an indication as to how that line would behave in the sun. Then again, Lockyer [3] carried out a lengthy investigation into the behaviour of lines of different lengths, and showed in the first place that there is no necessary connection between the intensity of a line and its length. He further showed that when metallic salts are examined it is the longest lines of the metal which appear most easily, and that the more easily the salt is dissociated the more of the shorter lines appear. As the concentration of an element is decreased the shorter lines disappear first until only the longest lines remain visible. This was subsequently taken up by Hartley and by de Gramont in their work on the persistence of lines and quantitative methods based thereon, which we dealt with in the preceding chapter. Amongst the results obtained by Lockyer may be included the fact that it is the longest lines which first show the phenomenon of self-reversal.

Reversal of Spectrum Lines.—By the reversal of a spectrum line is meant the process by means of which the line appears black on a bright background. This reversing process may be obtained in two ways: first, by causing a beam of light from an incandescent body to pass through the vapour of the substance, when the absorption or reversed lines are seen upon a continuous spectrum as background; 2nd, when the centre of a glowing mass of vapour is at a greater density than the outer layers, as, for example, in the arc. In this case the central portions emit a broadened line owing to the increased density, while the outer layers absorb some of these rays, and as they are much less dense than the central portions, they form

[1] See p. 204.
[2] *Proc. Roy. Soc.*, **18**, 79 (1869).
[3] *Phil. Trans.*, **163**, 253, 269 (1873); II., **164**, 479, 805 (1874).

only a very fine absorption line, so that an effect is produced of a fine black line in the centre of a broader bright line. This reversal is due to the difference of density of the two layers; if the emission and absorption were the same no lines would be seen. This phenomenon is known as self-reversal, and is especially visible in the spectra of the arc, where the necessary conditions most frequently occur. The ultra-violet lines are generally most easily reversed, and in photographs of arc spectra it will generally be found that the principal ultra-violet lines are self-reversed.

A great deal of work upon the reversal of lines has been done by Liveing and Dewar, and by Lockyer. Into this there is no need to enter, but certain points in connection with self-reversal may be considered. It will nearly always be found that self-reversal begins with the lines in the ultra-violet, and extends further into the visible spectrum as the conditions therefor are improved. Liveing and Dewar,[1] however, state that this is not the case with lithium, the lines of which reverse in the order—red, orange, blue, green, violet.

When an arc spectrum such as that of iron is photographed, very many lines will be found to be self-reversed; on the negative they appear as black lines with a very fine transparent centre. When the line is symmetrically reversed, the measurement of their centre is readily enough made by fixing the cross-wire in the eye-piece upon the centre of the reversed portion. In certain cases unsymmetrical lines are reversed, and then unsymmetrical reversal is obtained, and considerable errors in determination of the position of the line will ensue unless care be taken in the setting of the cross-wires. When the vapour of the substance is very dense in the arc, *i.e.* when a great deal of the substance is used, at times a multiple reversal shows itself; Jewell[2] explains this by the presence of a series of concentric layers of vapour of maximum and minimum density round the arc. One photograph of Jewell's showed four reversals in the magnesium line at $\lambda = 2852$; Kayser is inclined to view this effect on the plate as being due to a succession of changes of position of the reversal. Liveing and Dewar say, however, that they have seen the effect with the eye. In Fig. 65 is reproduced a portion of the arc spectrum of iron. This is enlarged from a photograph taken of the second order spectrum given by the Rowland grating at University College, London; an idea of the scale is shown by the wave-lengths of the lines; it is very nearly 1 cm. for 1 A.U., which would make the whole spectrum from $\lambda = 7600$ to $\lambda = 2000$, 560 metres long. The self-reversal is clearly shown in the four principal lines.

The self-reversal may also be seen in spark spectra, as, for example, in the case of cadmium when one or two of the lines in the ultra-violet are frequently found to be self-reversed. Similarly also it is easy to obtain the green line of mercury self-reversed when a discharge is passed through mercury vapour under low pressure. Wood[3] has

[1] *Proc. Roy. Soc.*, **35**, 76 (1883). [2] *Astrophys. Journ.*, **3**, 96 (1896).
[3] *Phys. Zeitsch.*, **7**, 926 (1906).

also obtained self-reversal of the red hydrogen line when the condensed spark discharge is passed through rarefied hydrogen in a vacuum tube with a long capillary portion which is viewed end on.

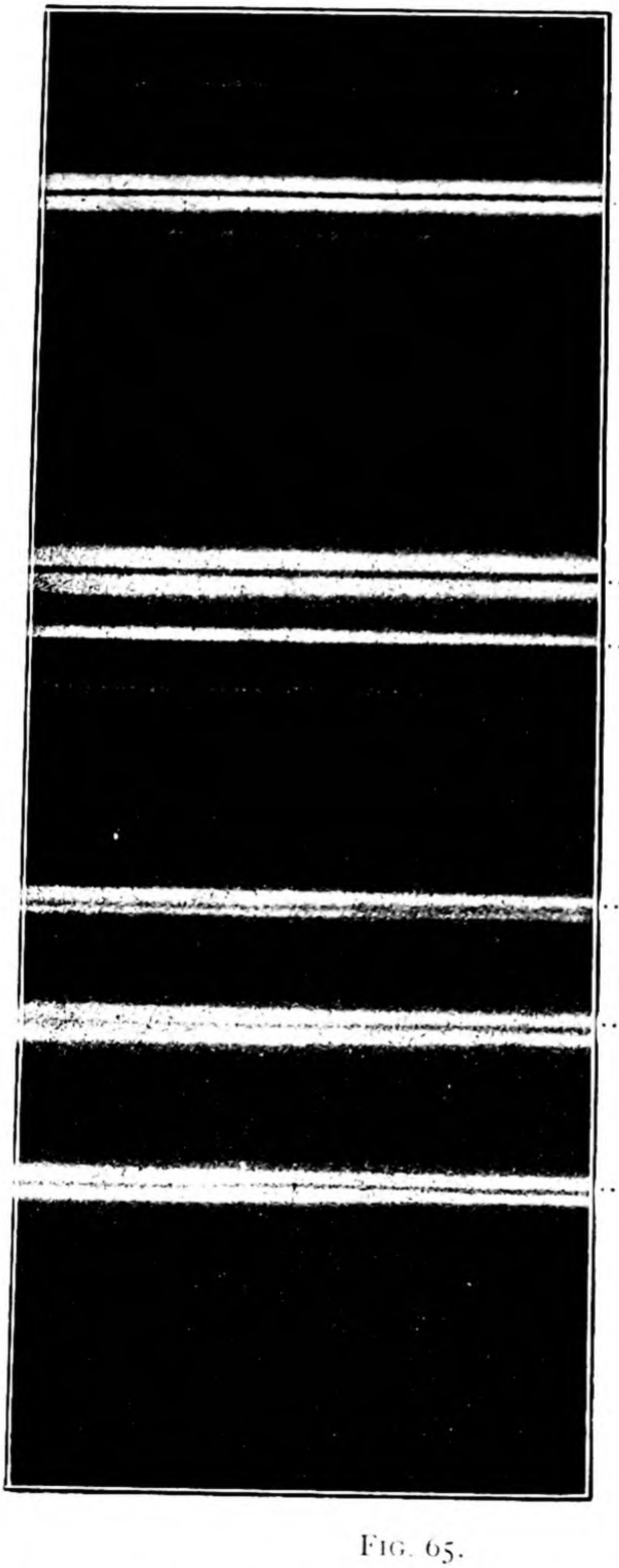


FIG. 65.

In connection with the general phenomenon of the reversal of lines the discovery of the stars, the spectra of which show both bright

and dark lines, is of great interest. A considerable number of these stars have been discovered since Wolf and Rayet first noticed the existence of three in 1867. This type of star is exemplified by ζ Puppis and λ Cephei, the spectra of which show the ionised helium lines at $\lambda = 5412, 4542, 4200, 4026, 3924, 3858, 3815$, together with the neutral helium line at $\lambda = 4471$ as dark lines, but the two lines at $\lambda = 4686$ and 4638 are bright. The first of these is due to ionised helium and the second is a blend of the two ionised nitrogen lines at $\lambda = 4634$ and 4643. Another type exemplified by 29 Canis Majoris also shows the last-mentioned two bright lines of ionised helium and nitrogen, together with the hydrogen lines, numerous helium lines, and other lines as dark lines.

The co-existence of both bright and dark spectrum lines is characteristic of the spectra of Novæ or new stars at certain stages of their development. It is not possible here to discuss the very fascinating problem of stellar spectra,[1] but with respect to the particular phenomenon now mentioned reference may be made to King's observations which were described on p. 80.

Plurality of Spectra.—Until the advent of the Bohr theory, considerable difficulty was met with in interpreting the variety in the spectra given by certain substances. For example, there are the two well-known spectra of hydrogen, the Balmer line spectrum and the complex secondary spectrum, the line and band spectra given by many metals, and the several band spectra due to carbon compounds. As the result of the Bohr theory, it has been quite definitely established that line spectra are due to elementary atoms and band spectra to compound molecules containing more than one atom. This at once introduced a simplification into a somewhat chaotic state of affairs, but there still remains a large unexplored field wherein much of great interest lies hidden. The term plurality of spectra, coined in the pre-Bohr epoch, may be retained as a convenient heading of this section, in which some account may be given of these most interesting phenomena.

Before the Bohr theory threw such clear light on the facts observed by spectroscopists, the complexity of the spectra exhibited by certain substances was extremely difficult of explanation, and although great advances have been made it cannot be said that a complete explanation has been found. It is not possible to do more than indicate the lines along which progress is being made, and for this purpose we may select the cases of hydrogen, oxygen, nitrogen, and carbon. In general, with a given element three or more different spectra can present themselves according to the circumstances. First, there is the spectrum due to the molecules, which will be a band spectrum; second, the spectrum of the free atoms, which will be a line spectrum containing series of the type characteristic of the relevant chemical family;

[1] See *Astronomical Physics*, p. 102 *et seq.*, by F. J. M. Stratton. Methuen, London, 1925.

and third, the enhanced spectra of the singly, doubly, etc., ionised atoms. It must be remembered that it is only in very few cases that the band spectra of diatomic or more complex elementary molecules have been observed, since such molecules rarely exist under the usual conditions of excitation. We have the well-known cases of the spectra of the hydrogen, oxygen, and nitrogen molecules, which are sufficiently stable to give their characteristic emission spectra, but in the case of the metals the vapours are in the majority of cases monatomic under normal conditions and they always give the characteristic line spectra of their atoms in the arc or spark discharge. The band spectra which are given by certain metals along with their line spectra are due to compound molecules, such as those of the hydride or oxide.

With reference to the statement above about the well-known spectrum of the hydrogen molecule, it must be pointed out that it is only quite recently that the molecular origin of this spectrum has been definitely established. This spectrum, which is usually called the secondary spectrum or sometimes the many-line spectrum of hydrogen, is familiar enough to all who have worked with vacuum tubes filled with this gas. It has at times been attributed by different observers to the hydrogen atom, to the water molecule, and to the hydrogen molecule. Difficulties are to be found in accepting any of those explanations. The atomic origin at once raises the question of the possibility of the hydrogen atom being able to emit two different spectra, and this now can be answered by a direct negative on the Bohr theory. The molecular origin raises a difficulty in that the spectrum does not present to the eye any of the characteristic structure of a band spectrum, all other molecular spectra having that structure. The problem, therefore, has been one of considerable interest, and the more recent work which has solved it may be given in some detail. The question of the structure of this spectrum in relation to the general laws of band spectra will be dealt with in Vol. III., Chapter IV.

On the experimental side considerable interest attaches to an investigation by R. W. Wood on the phenomena observed when the electric discharge is passed through hydrogen under reduced pressure in very long vacuum tubes.[1] This work is of importance because it has given very definite evidence in favour of the hydrogen molecule being the origin of the secondary spectrum and also because it has thrown some light on the actual phenomena which must take place when gases under reduced pressures are submitted to the action of the discharge.

As is well known, an ordinary vacuum tube containing hydrogen, when illuminated by a direct or alternating discharge, emits two spectra, namely, the Balmer lines and the secondary spectrum. As will be shown in Volume III., Chapter I., the former is characteristic of the hydrogen atom, which can only give a single series of lines, that is

[1] *Proc. Roy. Soc.*, A, **97**, 455 (1920); *Phil. Mag.*, **42**, 729 (1921); **44**, 538 (1922); *Proc. Roy. Soc.*, A, **102**, 1 (1922).

the Balmer series, so-called because Balmer showed that the wave-lengths of these lines can be expressed by a simple formula.

The presence of the secondary spectrum which contains many lines causes considerable trouble when attempts are made to obtain photographs of the Balmer series of lines, and indeed it is not possible under ordinary circumstances to trace this series beyond the twelfth member of the series. By the use of very long vacuum tubes of a simple design Wood succeeded in the first place in obtaining the Balmer spectrum free from contamination by the secondary spectrum and continuous background. The central portion of these tubes consists of a straight glass tube, 40 cm. long and 7 mm. internal diameter. At the two ends of this tube are attached two side tubes carrying the electrodes, and it is essential that the distance between the latter and the central portion be 80 cm. The discharge in the central portion is viewed end-on through a quartz window. For reasons which will be presently apparent, the tube must be free from internal scratches and from any solid particles.

When such a tube is filled with hydrogen at 0·5 mm. pressure and operated by either a direct or alternating current of high potential, the secondary spectrum appears only at the ends of the tube in the vicinity of the electrodes, the central portion showing the Balmer lines, with a faint trace of the secondary spectrum. Wood succeeded in obtaining photographs of the series as far as the 20th member, which has an intensity of about 1/600,000th of that of the red H_α line.

During the course of this work Wood noticed that bright white spots sometimes appeared along the central portion of the tube and that these spots showed the secondary spectrum of hydrogen with an intensity about fifty times that in adjacent portions of the tube, which gave the nearly pure Balmer spectrum. The accidental presence of a minute piece of sealing wax gave the key to the whole problem. Under the influence of the powerful discharge this fragment was almost immediately converted into a white spot of stannous oxide, and the secondary spectrum appeared at once in its vicinity. After a few minutes the oxide was reduced to metallic tin.

A fine tungsten wire, sealed into the side of the central portion of the tube, was raised to incandescence with again a strong appearance of the secondary spectrum in its neighbourhood. A thin thread of glass was not melted and consequently the incandescence of the tungsten wire could not have been due to the high temperature of the discharge. A small tungsten wire in a bulb attached to the side of the central portion of the tube was raised to a red heat, and this indicated that the heating effect is in all probability due to the re-combination of the dissociation products of the discharge.

A platinum wire when placed in the discharge remained non-luminous even with the most powerful discharges, but if the hydrogen was replaced by air then the wire became red-hot, probably by causing the re-combination of nitrogen atoms.

Mention should be made of the fact that during these experiments the vacuum tube was always in connection with the exhaust pump and pure electrolytic hydrogen was admitted into one end of the tube through a very fine and long capillary tube. Moist hydrogen was used, since water vapour is necessary for the production of the Balmer spectrum.

From the foregoing results it seems probable that the heating of the tungsten wire is due to the re-combination of hydrogen atoms to form molecules, as the very small amount of oxygen present can hardly account for the phenomenon.

When the discharge commences in the tube, the secondary spectrum flashes for a fraction of a second, the duration of this flash being from 0·01 second with 20 amperes in the primary of the transformer, to 0·04 second with 2 amperes. If the discharge is stopped for more than about 0·2 second, then the flash of the secondary spectrum can again be obtained when the discharge is passed. If the interruption is much less than 0·2 second, only the Balmer spectrum appears and consequently the normal interruptions of the discharge due to the passage of the transformer potential through the zero point are too brief to allow the restoration of the conditions for the secondary spectrum; in other words the hydrogen remains in the atomic state. During the passage of a powerful discharge, practically all the hydrogen in the central portion of the tube is in the atomic state, and hence only the Balmer lines appear.

The appearance of the secondary flash at the make and not the break of the current argues that the secondary spectrum is due either to the continuous excitation of the molecules or to their decomposition into atoms, and not to their re-combination to form molecules. There still, however, remains to be explained the fact that water vapour or oxygen is required to bring out the atomic spectrum. Wood used a tube containing a tungsten wire and a platinum wire sealed into the central portion and tried the effect of the addition of increasing quantities of oxygen obtained by heating some potassium permanganate in a side tube attached to the apparatus. With small quantities of oxygen the tungsten wire glowed at full incandescence, whilst the platinum wire did not glow at all. On increasing the quantity of oxygen the tungsten wire cooled and the platinum wire grew first red-hot and then white-hot. If the hydrogen were dried over phosphorus pentoxide neither wire became hot unless some oxygen were added.

The explanation of the phenomena caused by the oxygen is explained by Langmuir's work on the dissociation of hydrogen molecules into atoms by an incandescent wire. He drew Wood's attention to the remarkable power that oxygen possesses of poisoning such a catalyst as tungsten. If the incandescence of the tungsten wire in Wood's experiments is due to the heat evolved when the wire catalytically causes the hydrogen atoms to re-combine, then the action of oxygen in depressing the incandescence is readily explained.

The secret of obtaining the pure Balmer spectrum in the central portion of the tube lies in the use of a tube wall of zero catalysing power, and Wood found that the surface left on cooling fused glass possesses a relatively small catalysing power. Fused quartz is very little better than a pyrex glass surface. When, however, the inner surface of the central glass tube is ground with fine carborundum powder at a point near the centre, this portion of the tube always shows the secondary spectrum strongly with the Balmer series at low intensity. The temperature at the ground glass surface becomes high, the D lines of sodium being so strong that the discharge appeared yellow in spots. A bead of glass broken in two and suspended in the discharge gives a strong secondary spectrum in its vicinity, the D lines showing brilliantly close to the fractured surface.

Very striking effects too are shown by small fragments of thorium oxide (from a Welsbach mantle), which glow with intense brilliancy. Larger fragments give rise to strong secondary spectrum without, however, incandescing. If a tungsten wire is sealed in the tube and minute fragments of thoria are present, the latter glow brilliantly when the discharge commences. Presently the tungsten wire begins to act on the hydrogen atoms, the secondary spectrum appears, and the incandescent fragments of thoria in the immediate neighbourhood of the wire are extinguished.

Wood also showed that it is possible to observe the passage of hydrogen atoms for considerable distances along the tube connecting the vacuum tube to the exhaust pump. A tungsten wire is maintained at a red heat at 4 cm. from the discharge tube, whilst fragments of thoria are luminous at distances of 20 cm. or more. Since the velocity of the hydrogen along the tube is 1 metre a second, this shows that re-combination of the atoms to free molecules takes place within about 1/5th of a second.

The appearance of the secondary spectrum near the ends of these long vacuum tubes is due to the re-formation of molecular hydrogen by the catalytic action of the electrodes. It is probable that the action of water vapour or oxygen in suppressing the secondary spectrum and enhancing the intensity of the Balmer spectrum is due to the poisoning effect these substances have on the glass walls of the tube. Under ordinary circumstances the walls catalyse the re-combination of the atoms as fast as they are formed, but this action becomes materially reduced by water vapour.

Although the results obtained by Wood afford strong evidence in favour of the hydrogen molecule being the origin of the secondary hydrogen spectrum, that evidence is not quantitative, that is to say no information can be found from his observations as to the mass of the particle which is radiating that spectrum. This final proof has been given by Merton and Barratt,[1] who have used a very elegant method based on the measurement of the width of the lines. It must

[1] *Phil. Trans.*, A, **222**, 369 (1922).

be remembered that Buisson and Fabry [1] had previously come to the conclusion that the hydrogen atom is the radiating particle, basing their conclusion on their measurements of the order of interference at which the fringe systems vanish. This method was briefly indicated in an account of their observations on the great nebula of Orion (Chap. I., p. 44). The relation used by them was—

$$N = 1{\cdot}22 \times 10^6 \times \sqrt{\frac{m}{T}}$$

where N is the order of interference when the fringe system vanishes, m is the mass, and T the absolute temperature of the radiating particles. This relation was developed by Schönrock [2] and also by Lord Rayleigh,[3] and the limit of visibility of the fringes depends on the width of the lines. Merton and Barratt determined the "half-width" of three lines of the secondary spectrum with great accuracy.

Now the distribution of intensity in a spectrum line when the sole cause of broadening is the motion of the radiating particles in the line of vision [4] is given by—

$$I = I_0 e^{-kx^2}$$

where I_0 is the maximum intensity, I is the intensity at a difference of wave-length x from the point of maximum intensity, and k is a constant depending on the mass and absolute temperature of the radiating particles. Lord Rayleigh showed that if $\delta\lambda$ be the "half-width" of the line, that is the value of x when $I/I_0 = 1/2$, then—

$$\frac{\delta\lambda}{\lambda} = 3{\cdot}57 \times 10^{-7}\sqrt{\frac{T}{m}}.$$

From this the relation used by Buisson and Fabry is derived.

The method adopted by Merton and Barratt was to calculate the half-width from measurements of photographs of the lines as obtained with an echelon grating, very high resolving power being essential. The echelon grating used by them consisted of thirty-five glass plates, each being 15 mm. thick. The procedure consists in taking photographs of the line under investigation, first with the grating in the double order position and then in the single order position, the conditions of excitation of the hydrogen and the exposure being identical in the two. The photographs were developed with hydroquinone and potash, which give very great contrast, and the negative was then given a mild treatment with a solution of potassium ferricyanide, this effecting a contrast so great that the edges of the lines could be measured to within a few thousandths of a millimetre.

The theory of the method may be understood from Fig. 66, where

[1] *Journ. de Phys.*, **2**, 442 (1912). [2] *Ann. der Phys.*, **20**, 995 (1906).
[3] *Phil. Mag.*, **29**, 274 (1915).
[4] This phenomenon, known as the Doppler effect, will be discussed in Vol. IV.

the upper curve represents the distribution of intensity by the echelon grating which is given by—

$$I_n = \frac{\sin^2 \alpha}{\alpha},$$

where $\alpha = \pi\theta\sigma/\lambda$, θ is the angle of diffraction, and σ is the width of the grating step. Immediately below the upper curve is shown the intensity curve of a spectrum line as seen in the single order position, and the two intensity curves as obtained with the line in the double order position. Since the intensity distribution is superposed, the observed intensity distribution is not exactly the same as the true intensity distribution given by $I = I_0 e^{-kx^2}$. The two strips in the lower portion of Fig. 66 show the appearance of the line as seen in the photographs of the single and double order positions. If it be

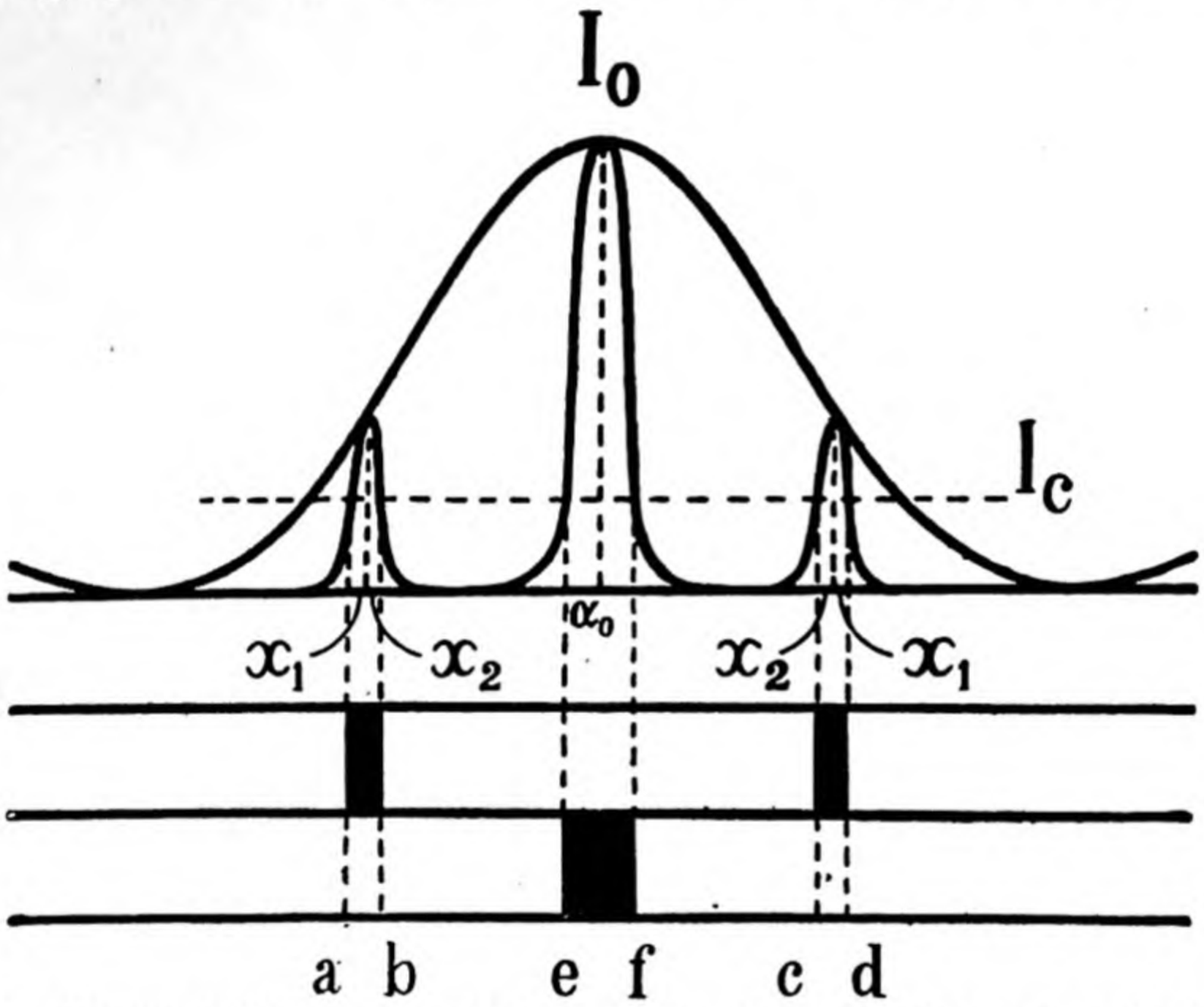


FIG. 66. (From *Phil. Trans.*, Vol. A, 222. Paper by Merton and Barratt.)

assumed that a constant photographic density is given by a light of a constant (but unknown) intensity, then the edges of the lines on the photographic plate will denote a certain critical intensity of light. This is represented by the dotted line I_c in the upper part of Fig. 66.

Let x_1 and x_2 denote the distances of the edges *a* and *b*, or *c* and *d*, respectively, from the true point of maximum intensity of the line in the double order position, where $x = 0$ and $\alpha = \pi/2$, and let α_0 denote the distance of the edges *e* and *f* from the maximum in the single order position, where $x = 0$ and $\alpha = 0$. Then, if x and α_0 are expressed in circular measure, we have for the double order position

$$\begin{cases} \frac{I_c}{I_0} = \frac{\sin^2 \alpha_1}{\alpha_1^2} e^{-kx_1^2} \quad . \quad . \quad . \quad . \quad (1) \\ \frac{I_c}{I_0} = \frac{\sin^2 \alpha_2}{\alpha_2^2} e^{-kx_2^2} \quad . \quad . \quad . \quad . \quad (2) \end{cases}$$

and for the single order position—

$$\frac{I_c}{I_0} = \frac{\sin^2 a_0}{a_0^2} e^{-kx_0^2} \quad . \quad . \quad . \quad . \quad (3)$$

where a_1 and a_2 are the angles corresponding to the points a and b, or d and c, respectively.

If we put

$$\frac{\sin^2 a_0}{a_0^2} = R, \quad \frac{\sin^2 a_1}{a_1^2} = P, \quad \text{and} \quad \frac{\sin^2 a_2}{a_2^2} = Q,$$

then $$\log\left(\frac{R}{P}\right) = k(a_0^2 - x_1^2) \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

and $$\log\left(\frac{R}{Q}\right) = k(a_0^2 - x_2^2) \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

In reading the plates with a micrometer, the positions of the points, a, b, c, d, e, f, are expressed in an arbitrary scale. Further, the measured distance between a and c, or between b and d, does not represent an angle n, because x_1 is not exactly equal to x_2. Owing to the fact that it is not possible to find in terms of our arbitrary scale the separation of two successive orders, both equations (4) and 5) must be used in order to determine the value of k. Merton and Barratt proceed as follows: The measurements give $2a_0$ and $(x_1 + x_2)$ in terms of the arbitrary scale, that is in micrometer divisions, and it is necessary to find a value of $x_1 - x_2$ such that equations (4) and (5) give the same value of k, from which the value of the half-width, $\delta\lambda$, at once follows, since the difference in wave-length corresponding to the separation of successive orders is known from the optical constants of the echelon grating. The value of $x_1 - x_2$ is very small and can readily be found by trial of a series of values, which can be plotted against the resulting values of $k_{\text{from (4)}} - k_{\text{from (5)}}$ on squared paper.

Merton and Barratt measured in this way the half-widths of the lines $\lambda = 6225$, 6028, 6018, and also the half-width of the helium line $\lambda = 5015$ as a check on the accuracy of the method. The choice of lines in the secondary spectrum for measurement of their half-widths is limited on the one hand by their intensity, and on the other hand by their complete isolation from adjacent lines by the constant deviation spectroscope used to separate the lines before examination by the echelon grating. The exposure time was made as short as convenient in order to guard against any temperature change in the echelon.

The next point which concerns us is the temperature of the radiating particles. Merton and Barratt first of all passed the discharge through the vacuum tube for a considerable time in order to secure the establishment of a state of equilibrium between the heating of the gas by the discharge and the cooling of the walls of the tube by radiation and convection. It is obvious that when the equilibrium has been reached, the temperature of the outer wall of the central

capillary portion must be somewhere between the temperature of the radiating gas and that of the room. By placing on the outer wall of the capillary specks of various organic compounds of known melting-point and observing which of these melted and which did not melt, the temperature of the glass walls is determined. Assuming that the interchange of energy between the walls and the surrounding air is by radiation only we obtain a lower limit to the temperature of the radiating gas. It is also assumed that the conduction of the glass walls is infinitely large compared with that of the radiating gas and of the surrounding air. We then have for the absolute temperatures—

$$T^4_{gas} - T^4_{glass} = T^4_{glass} - T^4_{air}$$

from which the absolute temperature of the radiating gas can at once be found. It is very important to note that all the assumptions made tend to give an inferior limit to the temperature of the radiating gas, for the lower this limit, the smaller will be the value found for the mass of the radiating particle. Furthermore, any loss of definition due to the optimum conditions of adjustment of the apparatus not being realised will increase the values found for the half-widths of the lines. It follows that when the values for the half-widths and the absolute temperature have been determined in the manner described, the masses of the radiating particles must exceed a certain specified amount.

In the actual experiments it was found that the temperature of the walls of the capillary tube was just sufficient to melt cinnamic acid. This temperature, therefore, was 406° abs. and the temperature of the radiating gas was calculated to be 456° abs. In Table XXXIV. are given the observed values of the half-widths of the three hydrogen lines and the helium line, together with the calculated values. In the case of the helium line the temperature of the radiating gas was probably somewhat higher than 456° abs., since the capillary wall was much thicker than in the case of the hydrogen tubes.

The calculated value of the half-width of this line, however, was obtained on the assumption that the temperature was 456° abs.

TABLE XXXIV.

		$\delta\lambda_{obs.}$	$\delta\lambda_{obs.}$ mean.	$\delta\lambda_{calc.}$ for atom.	$\delta\lambda_{calc.}$ for molecule.
H_2	6225	0·034, 0·033, 0·038, 0·039, 0·032	0·035	0·046	0·032
	6028	0·032, 0·033, 0·032	0·032	0·046	0·032
	6018	0·037, 0·036, 0·034, 0·030	0·034	0·048	0·034
He	5015	0·024, 0·022	0·023	0·019	—

The agreement between the observed values and those calculated for the H_2 molecule is extremely good, and it is interesting to note that the lines $\lambda = 6225$ and 6018 belong to the Fulcher series, are enhanced

at low pressures, and are weakened when a condensed discharge is used. Neither of these lines shows the Zeeman effect. The line $\lambda = 6028$ belongs to a different class, for it is enhanced by a condensed discharge and shows the Zeeman effect. Since these two classes are the most important in the secondary spectrum of hydrogen, it would seem that the whole of this spectrum has its origin in the hydrogen molecule as the radiating entity.

Apart from the fact that the small difference between the calculated and observed values of the half-width of the helium line may be very probably explained by too low an estimate of the temperature, Merton and Barratt believe that the limiting theoretical widths of lines are more nearly attained in tubes with wide capillaries in which the current density is lower. The vacuum tube used for the helium observations had a much narrower capillary than was used in the case of hydrogen.

As the result of this work no possible doubt can remain concerning the origin of the hydrogen secondary spectrum, the evidence being conclusive in favour of this spectrum being characteristic of the hydrogen molecule. The observations made by Buisson and Fabry, therefore, must be questioned and it is satisfactory to note that Duffieux,[1] on the request of these authors, has repeated their observations and found them to be subject to correction. As was stated above, Buisson and Fabry measured the width of the secondary spectrum lines by the method of determining the order of interference when the fringe systems vanish. The difference of path in the interferometer is increased until the visibility of the fringes reaches a critical value and then the mass of the radiating particles is determined from the order of interference N by the relation—

$$N = 1{\cdot}22 \times 10^6 \sqrt{\frac{\overline{m}}{\overline{T}}}.$$

The choice of the critical limit of the visibility in these observations is somewhat arbitrary. As was shown in Chapter I., p. 5, the visibility of a fringe system is given by—

$$\frac{I_1 - I_2}{I_1 + I_2}$$

where I_1 is the intensity at the centre of a bright fringe and I_2 the intensity at the centre of the adjoining dark fringe. The critical limit of 1/40 for the visibility adopted by Lord Rayleigh is a minimum value obtained under the most favourable conditions, which are rarely realised in practice. Fabry and Buisson from their observations on the rare gases adopted the value 1/16, and this appears to be very satisfactory for lines of reasonable intensity. Duffieux observed the fringes given by étalons of small thickness, for which the coefficient of reflection at normal incidence was very small. The

[1] *Comptes Rendus*, **176**, 1876 (1923).

visibility of such fringe systems can be calculated ; for instance, with an étalon having plain quartz plates, the visibility very near to the limit is very close to 1/12·5.

He shows that if these three values for the visibility be used, the following values are obtained for the order of interference which will be observed with the atoms and molecules of hydrogen :—

Visibility.	Order of interference	
	H.	H_2.
$\frac{1}{12·5}$	62000	88000
$\frac{1}{16}$	70500	100000
$\frac{1}{40}$	82000	116000

Duffieux used vacuum tubes with large electrodes and a short capillary tube, the radiation being viewed end-on. The capillary tube was immersed in a stream of water and the temperature of the radiating hydrogen was assumed to be that of the surrounding water. The order of interference obtained with the following lines was about 83,000, the visibility being comparable with that of the fringes given by a plane parallel quartz plate :—

6224	6098	6081	5938	5884
6199	6095	6032	5931	5883
6135	6091	5975	5888	5849

The two lines at $\lambda = 6121$ and 6018 gave an order of interference up to 95,000. . The following lines gave an order of interference up to 97,000 :—

4849	4764	4741	4684	4659	4617
4798	4743	4719	4663	4634	4568
4797	4743	4687	4661	4628	4554

It is evident therefore that all these lines must be attributed to the molecule of hydrogen.

The order of interference obtained by Buisson and Fabry was not greater than 72,000, and the principal explanation of this small value is doubtless to be found in the small dispersion of the spectroscope used in the preliminary analysis of the light from the discharge. Owing to this, blends of closely situated lines were examined with the étalon.

We may now return again to Merton and Barratt's work and consider some observations made by them in connection with the grouping of the lines of the secondary hydrogen spectrum in classes. It was

shown in an earlier paper by Merton [1] that the relative intensities of the lines of this spectrum are affected by the pressure, the groups known as the Fulcher bands [2] being enhanced at low pressures, and that a very striking change is caused by the admixture of helium with the hydrogen. The effect of the helium is greatly to enhance some of the lines and to bring a number of new lines into being, a second class of lines being unaffected, whilst a third class suffered a marked reduction in intensity. Then again, the lines have been classified in two other ways. Dufour [3] found that in a magnetic field some of the lines exhibit the Zeeman effect, whilst others are not affected, and these results were discussed by Fulcher in his assignment of some of the lines to bands. The Stark effect, that is to say the resolution of the lines into components in an electric field, is shown by 54 lines of the secondary hydrogen spectrum. The consideration of these two phenomena, namely, the Zeeman and Stark effects, cannot be taken up here,[4] but it may be accepted that each affords a method of classification of the lines in a spectrum such as the one with which we are now concerned.

In their experimental work Merton and Barratt used a vacuum tube with a central capillary portion 20 to 50 cm. long and 5 to 8 mm. internal diameter. The electrodes were spirals of aluminium ribbon, and there was a side tube to each vacuum tube into which was sealed a short platinum tube attached to a palladium tube. Pure hydrogen could be admitted into the vacuum tube by heating the palladium tube in a flame or in a current of hydrogen. The current was obtained from a large induction coil or from a 15,000 volt 1/4 kilowatt transformer. The capillary portion of the vacuum tube was viewed end-on through a thin glass window, there being no need for the use of quartz, since the lines do not appear to extend beyond $\lambda = 3368$.

The measurements of the wave-lengths of the lines were made with great care, the probable error being less than 0·02 Å. The total number of lines measured between $\lambda = 6540{\cdot}53$ and $3368{\cdot}47$ is 1130, and their wave-lengths are given in I.A. The lines are classified according to the effects caused by change in pressure, introduction of helium, and the condensed discharge. The standard condition under which the intensities of the lines were determined was a pressure of a few millimetres, the hydrogen being excited by the uncondensed discharge. For the effect of pressure the spectrum was examined at pressures of above 5 mm. and a very low pressure at which the walls of the vacuum tube showed a vivid green fluorescence. The classification is based on the increase or decrease of intensity shown by many of the lines under these two extreme conditions.

[1] *Proc. Roy. Soc.*, A, **96**, 382 (1920).
[2] *Astrophys. Journ.*, **34**, 388 (1911); **37**, 60 (1913); these bands will be discussed from the point of view of emission band spectra, in Vol. III., Chapter IV.
[3] *Ann. Chim. Phys.*, **9**, 361 (1906); *J. de Phys.*, **8**, 258 (1909).
[4] See Vol. III., Chapters II. and III.

Following up Merton's earlier observations, the changes of intensity exhibited by some of the lines on the admission of helium up to pressures of 40 mm. and more into the tubes were observed. As regards the effect of the introduction of a condenser and spark gap into the discharge circuit it is well known that in general this causes the secondary spectrum to change into the Balmer spectrum. Merton and Barratt noted, however, that when a condensed discharge of small voltage is passed through the vacuum tubes a group of lines between $\lambda = 6000$ and $\lambda = 5600$ becomes very prominent. It is true that these lines are decreased in intensity when the condenser and spark gap are introduced, but they are strong in relation to the remaining lines of the spectrum.

The different methods of classification, including the Zeeman and the Stark effects, are related to one another, but there are many exceptions to any broad generalisation. In the red and yellow regions all those lines which show the Zeeman effect are high-pressure lines, that is to say they are enhanced by increase of pressure, and most of them are strengthened when the condensed discharge is used. Many of these lines, but not all of them, are enhanced by the presence of helium. Again, the Fulcher band lines are essentially low-pressure lines, that is to say they are enhanced at low pressures, and they are weakened in the condensed discharge. To this rule there are six exceptions, namely, the lines at $\lambda = 6197{\cdot}05$ and $5317{\cdot}90$, which are high-pressure lines, and those at $\lambda = 6093{\cdot}83$, $5989{\cdot}22$, $5552{\cdot}52$, $5543{\cdot}41$, which are enhanced by the condensed discharge, $\lambda = 5989{\cdot}22$ also being a high-pressure line.

In general, the condensed discharge enhances the high-pressure lines and weakens the low-pressure lines, and the former are also enhanced by the admixture of helium. There are exceptions to this generalisation, the changes in intensity amongst these exceptions varying greatly in magnitude. Merton and Barratt believe that these exceptions in part at any rate may be explained by the assumption that the lines are close unresolved doublets.

So far as the Stark effect is concerned there appears to be no relation between this and the other methods of classification. It is of some interest that in the present work no evidence was found of the existence of the five lines at $\lambda = 4185{\cdot}4$, $4123{\cdot}9$, $4021{\cdot}7$, $3927{\cdot}3$, and $3846{\cdot}0$, quoted amongst the secondary hydrogen spectrum lines which show the Stark effect. Assuming that these lines are not due to impurities, they probably belong to that class of lines which only appears in very powerful electric fields. According to the Bohr theory the emission of a spectrum line is due to the return of an electron to its normal orbit from an orbit to which it has been displaced as the result of the excitation of the atom. Though there are many orbital changes which are geometrically possible, these are normally limited by what is known as the principle of selection. This principle is invalidated when the atom radiates within a powerful external field, with the result that new lines become visible under these circumstances.

The same principle applies to molecular vibration and rotation spectra, to which the secondary hydrogen spectrum in all probability conforms.[1]

There remains one other observation made by Merton and Barratt which may be mentioned. Following up an earlier observation made by Merton,[2] they found that it is possible to effect a separation of the gases in their vacuum tubes, the hydrogen tending to collect near the electrodes and the helium or mercury vapour in the capillary portion. This phenomenon had been observed some years previously[3] with mixtures of hydrogen and carbon dioxide. When the current is passed through the mixed gases at about 0·75 mm. pressure in a plain cylindrical tube 1 inch in diameter the discharge is white in colour and shows the spectra of the two gases, that is to say, the Balmer lines and the Ångström carbon bands. After a few seconds the negative glow changes to a pink colour and the positive column exhibits well-marked striations. This change is accompanied by a disappearance of the hydrogen lines from the positive column and their marked strengthening in the negative glow. If the current is switched off and the tube

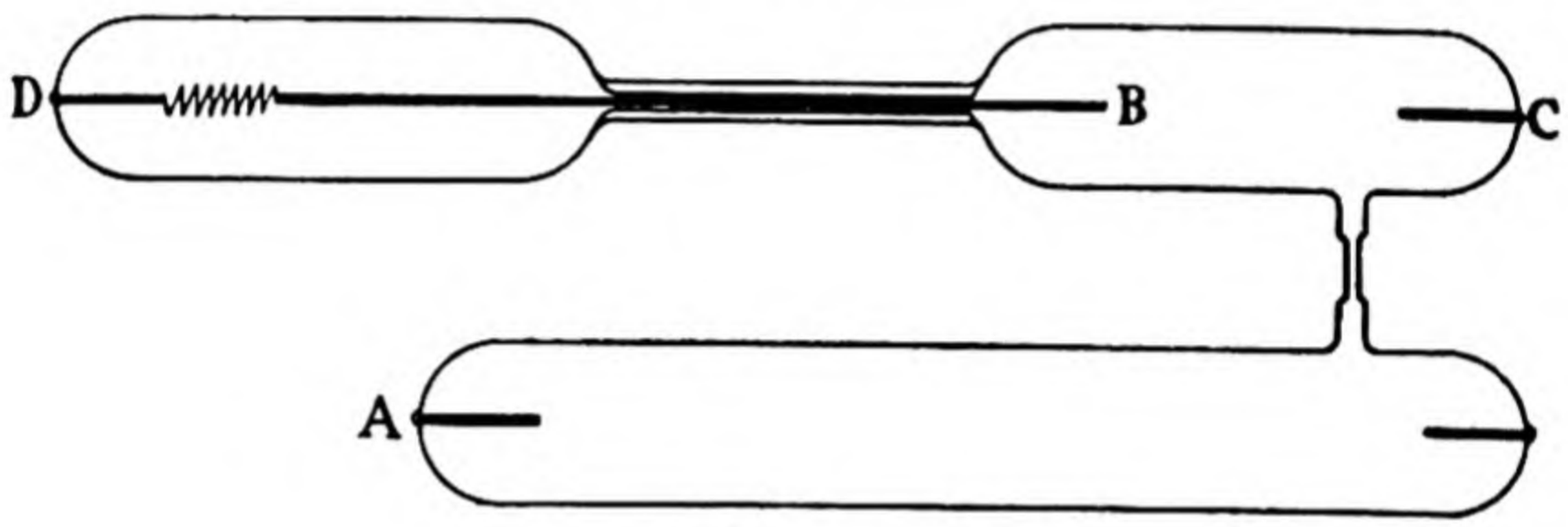


FIG. 67.

allowed to rest for about an hour, the same phenomenon is observed when the discharge is again passed through the tube.

It is possible to separate the hydrogen from the carbon dioxide by the use of the apparatus shown in Fig. 67. The electrode B consists of a stout copper wire, which is a little smaller in diameter than the capillary tube, and is attached by a spiral of fine platinum wire to a thicker platinum wire sealed in at D. The whole apparatus is filled with a mixture of hydrogen and carbon dioxide at about 0·7 mm. pressure, and the copper wire is brought into contact with the platinum electrode C. The discharge is then passed for some time, the copper wire being made the cathode and A the anode, after which the connecting neck between the two tubes is sealed off. The copper wire is then caused to take up the position shown in Fig. 67 and the spectra given by the two tubes compared. The tube A shows only a trace of hydrogen, whilst the tube containing the copper electrode shows it strongly. The same results are obtained when the hydrogen is mixed with nitrogen, sulphur dioxide, or carbon monoxide.

The emission spectra of oxygen present considerable interest, both

[1] See Vol. III., Chapter I.
[2] *Proc. Roy. Soc.*, A, **98**, 255 (1920).
[3] Baly, *Phil. Mag.*, **35**, 200 (1893); J. J. Thomson, *Nature*, **52**, 454 (1895).

on account of the various stages of ionisation that have been observed and also on account of their astrophysical importance. When an uncondensed discharge is passed through a vacuum tube containing oxygen two spectra may be observed, a line spectrum in the capillary portion of the tube and a band spectrum in the negative glow. The latter was first recorded by Wüllner [1] and is without doubt due to the oxygen molecule.

In 1879 [2] Schuster showed that there are two different line spectra given by oxygen in vacuum tubes, namely, the one mentioned above which he called the compound line spectrum, and a second or elementary line spectrum when a condensed discharge is used. These names were given because it was believed that complex and simplified molecules were involved in the production of these two spectra. The elementary line spectrum had previously been observed by Plücker.[3] The compound line spectrum was resolved into series of lines by Runge and Paschen,[4] and we now know that this spectrum is characteristic of the neutral oxygen atom.

For many years these remained as the only facts known about the emission spectra of oxygen, with the exception that certain new lines were observed which indicated the existence of a third line spectrum, these new lines appearing when more powerful condensed discharges were employed. In view of what has been said about the spectra of the ionised atom, it is not surprising to learn that the so-called elementary line spectrum is due to the singly-ionised oxygen atom, and it is of very great importance that this spectrum has been analysed by Fowler [5] and arranged in series.

The third line spectrum mentioned above is that of the doubly-ionised oxygen atom, but as yet a complete analysis has not been published. This spectrum has been investigated by Lunt [6] and by Fowler and Brooksbank.[7] Evidences of the spectra of the oxygen atom in two higher stages of ionisation have been obtained by Millikan and Bowen.[8]

There have thus been recognised six spectra of oxygen, namely, those characteristic of O_2, O, O^+, O^{++}, O^{+++}, and O^{++++}. Of these only those of O and O^+ have been fully analysed from the series standpoint, and it is very interesting to note the essential difference between the two. The spectrum of the neutral atom belongs to a system of odd multiplicities, whilst the spectrum of the singly-ionised atom belongs to a system of even multiplicities. The series in the former consist of singlets and triplets, whilst in the latter they consist of doublets and quartets. The fundamental significance of this will

[1] *Pogg. Ann.*, **144**, 481 (1872). [2] *Phil. Trans.*, **170**, 37 (1879).
[3] *Pogg. Ann.*, **107**, 518 (1859).
[4] *Ann. der Phys.*, **61**, 641 (1897); *Astrophys. Journ.*, **8**, 70 (1898).
[5] *Proc. Roy. Soc.*, A, **110**, 476 (1926).
[6] *Annals of the Cape Observatory*, **10**, II., 26 B (1906).
[7] Royal Astronomical Soc., *Monthly Notices*, **77**, 511 (1917).
[8] *Phys. Rev.*, **24**, 209 (1924).

be discussed in Vol. III., Chapter I., and it is mentioned here in order to show the essential difference between the two spectra.

The spectra of the nitrogen atom and molecule exhibit a further complexity in that there is a plurality in the band spectra of the latter. The first observations of the spectra of nitrogen were made by Plücker and Hittorf [1] with vacuum tubes filled with this gas. They found that with the ordinary uncondensed discharge two different band spectra are visible, one in the capillary portion of the tube and the other in the negative glow. The former was given the name of the positive band spectrum, whilst the latter was given the name of the negative band spectrum. Plücker and Hittorf further considered that the positive spectrum consisted of two superimposed spectra, namely, the first positive band spectrum which consists of a series of bands degraded towards the blue and extending from $\lambda = 7636$ to $\lambda = 5100$, and the second positive spectrum which also consists of bands degraded towards the short wave-lengths and extends from $\lambda = 5069$ to $\lambda = 3000$. It was also found that when a condensed discharge is used a line spectrum is obtained.

The band spectra of nitrogen are familiar to all those who work with vacuum tubes, since they appear whenever air or nitrogen is present. The capillary portion of the tube, or more accurately the positive column of the discharge, glows with a fine orange colour, the negative glow having a blue colour. When the spectrum of the positive column is examined, it can be seen that bands in the orange have not the same appearance as those in the blue, and it was for this reason that Plücker and Hittorf considered that the two sets of bands belonged to two different spectra. The bands of the negative spectrum are again degraded on their more refrangible sides and have a structure which is very different from that of the two positive band spectra.

The contention of Plücker and Hittorf as to the individuality of the two band spectra has been completely verified by Deslandres,[2] who has proved that different formulæ are required to represent their structure. Definite experimental support of this has also been recorded. For example, in the preparation of argon from the atmosphere one of the methods for the removal of the last traces of nitrogen is to pass sparks through the gas, mixed with oxygen, over potash solution, when the nitrogen is oxidised and absorbed. The excess of oxygen is subsequently removed by burning phosphorus. If, as sometimes happens, the sparking process has not been carried quite far enough and a minute amount of nitrogen is left, this reveals itself when a vacuum tube is filled with the gas. Under these circumstances the negative glow spectrum is not visible, but only the positive band spectra which are separated, the first positive spectrum being given by the capillary portion, and the second by the negative glow.

A somewhat similar observation has been made by Goldstein,[3]

[1] *Phil. Trans.*, **155**, 1 (1865).
[2] *Comptes Rendus*, **101**, 1256 (1885); **134**, 747 (1902); **138**, 317 (1904).
[3] *Phys. Zeitsch.*, **6**, 14 (1905).

who filled a cylindrical vacuum tube, about 3 cm. in diameter, with nitrogen at a few cm. pressure. The discharge through the gas is then very narrow and shows the two positive band spectra in the positive column. When the whole discharge tube is immersed in liquid air the positive column increases in diameter and changes colour to a greenish-yellow. The spectrum finally shows only the first positive band group, the blue bands being entirely absent.

As will be more fully explained in Vol. III. one of the important methods of excitation of atoms and molecules is by means of electrons travelling with definite and known velocities. The first quantitative observations with nitrogen were made by Fulcher,[1] who found that as the velocity of the electrons was increased the positive band spectra first appeared and that with higher velocities the negative bands appeared. This result was subsequently confirmed by Foote and Mohler,[2] who found that the positive bands were obtained when the potential gradient was 7 volts and that the negative bands were strongly developed when the potential gradient was 25 volts.

As regards the line spectra of the nitrogen atom, it is only recently that any progress has been made in their recognition and differentiation. From what has already been said with reference to the spectra of neutral and ionised oxygen atoms, it is to be expected that there should exist at any rate three line spectra of nitrogen, namely, those of the neutral, singly-ionised, and doubly-ionised atoms. The probable existence of these three types was pointed out by Fowler [3] and as the result of subsequent developments, it is probable that the spectrum of the neutral atom will exhibit series which belong to systems of even multiplicities, whilst those of the singly- and doubly-ionised atoms will belong to systems of odd and even multiplicities, respectively.

The line spectrum which is given by the spark discharge through nitrogen in vacuum tubes, contrary to what might be expected from analogy with oxygen, is not the spectrum of the neutral nitrogen atom, but that of the singly-ionised atom. The same spectrum is given by the condensed spark in air at atmospheric pressure, the well-known air lines of nitrogen belonging to this spectrum. This spectrum has been examined by Fowler,[4] who shows that the series terms are single and triple, that is to say, they belong to a system of odd multiplicities as was expected. As yet no analysis of the spectrum of the doubly-ionised atom has been published, although Fowler has been able to assign a number of lines to this spectrum.[5]

It is very remarkable that the line spectrum of the neutral nitrogen atom or the arc spectrum, as it may be called, remained undiscovered for so long a time. The first observations of this spectrum were made

[1] *Astrophys. Journ.*, **37**, 60 (1913). [2] *Origin of Spectra*, p. 191.
[3] *Report on Series in Line Spectra*, p. 165, Fleetway Press, London, 1922.
[4] *Proc. Roy. Soc.*, A, **107**, 31 (1925).
[5] Royal Astronomical Soc., *Monthly Notices*, **80**, 692 (1920).

by Hardtke[1] in 1918, who noted thirty-eight lines which were present in the spectrum of the positive rays in nitrogen-filled vacuum tubes, and he assigned them to the missing nitrogen spectrum. More recently, Merton and Pilley[2] have succeeded in obtaining this spectrum free from contamination by the enhanced lines, and this investigation is one of considerable interest.

In the account given above of Merton and Barratt's work on the secondary spectrum, reference was made to the marked influence exerted by the presence of helium. This effect is particularly noticeable when a small quantity of hydrogen is present in a tube containing helium at a comparatively high pressure. As will be discussed below Merton and Johnson observed profound modifications in the spectra of carbon caused by helium, one of these confirming an earlier observation by Fowler. Merton and Pilley used the same method and studied the spectra given by a trace of nitrogen in the presence of helium at higher pressures, and it was in this way that they were able to secure the conditions necessary for the production of the arc spectrum of nitrogen. It was found, however, that the preparation of the vacuum tubes entailed much greater difficulties in the case of nitrogen than in the cases of hydrogen and carbon.

For the investigation of the nitrogen lines the carbon spectrum must be eliminated, and when the pressure of the helium is as great as 30 mm. this is a difficult matter. A procedure which would yield helium tubes showing no trace of any impurity at 5 mm. pressure generally results in a brilliant comet-tail spectrum when the pressure is increased to about 30 mm. This comet-tail spectrum is one of those due to carbon and will be described below. The tubes used by Merton and Pilley were of the H form, with spiral aluminium electrodes and tubes 8 to 12 mm. in diameter in place of the usual capillary. Each tube was provided with a series of side tubes and into one of these was sealed a platinum tube attached to a palladium tube for admitting and removing hydrogen. The remaining side tubes were attached to bulbs containing, respectively, phosphorus pentoxide, lumps of caustic potash, potassium permanganate, and lastly alumina which had been moistened with a dilute solution of sodium azide and dried at a moderate temperature. In a separate side tube was sealed a short length of platinum wire with a small bead of silver fused on to the end. When the discharge was passed between one of the aluminium electrodes and this silver electrode a deposit of silver was formed on the walls and this effectively removed all traces of mercury vapour.

Before the side tubes were sealed on the tubes were washed out with dilute hydrofluoric acid, followed by distilled water, as this was found to be by far the most effective method of cleaning them. The helium was stored in an ordinary gas generator, and this was connected to the vacuum tube through a large U-tube containing cocoa-

[1] *Ann. der Phys.*, **56**, 363 (1918).
[2] *Proc. Roy. Soc.*, A, **107**, 411 (1925).

nut shell charcoal. The exhaustion was carried out by means of a mercury vapour pump backed by an oil pump and the discharge tube and the charcoal tube were strongly heated during the process.

A heavy discharge was passed at intervals through the tubes, which were washed out from time to time with oxygen by heating the potassium permanganate. The charcoal tube was then immersed in liquid air, and helium was passed very slowly through it into the discharge tube until the pressure of about 30 mm. was reached. The discharge tube, which showed a strong comet-tail spectrum, was then sealed off, since the charcoal appeared to be unable to absorb the source of this spectrum. The last traces of carbon compounds were removed by admitting oxygen and by passing a heavy discharge for a considerable time, when presumably they were oxidised to carbon dioxide and absorbed by the caustic potash. At the same time nearly all the hydrogen was eliminated by absorption as water vapour by the phosphorus pentoxide, and the excess of oxygen was taken up by the electrodes.

The tube was then ready for the admission of nitrogen by heating the alumina and sodium azide, and this operation required great care owing to the difficulty of controlling the amount admitted. With any excess the spectrum shows only the positive and negative bands, and the helium lines when a condensed discharge is used. Merton and Pilley do not discuss in the present paper the phenomena observed with the uncondensed discharge and content themselves with the statement that the band spectra of nitrogen only are observed, these spectra being in some respects modified by the helium, the negative bands being greatly enhanced in intensity.

When a condenser and a small air gap are introduced into the discharge circuit an entirely different series of phenomena are observed. With nitrogen in excess only the band spectra are visible, as already noted, and when the nitrogen has been absorbed by the electrodes the tubes only show the line and band spectra of helium, together with traces of the neon lines. In between these two extremes there lies an intermediate stage, when the tube contains an extremely small quantity of nitrogen, in which the nitrogen and helium band spectra are both much weakened and a line spectrum appears. This spectrum is entirely different from the ordinary spark spectrum of nitrogen, which as stated above is that of the singly-ionised atom, and its strongest lines are not conspicuous even when condensed discharges are passed through nitrogen-filled vacuum tubes. This spectrum includes the lines observed by Hardtke, but under the present conditions the new spectrum is quite isolated from the well-known spark spectrum. With very intense discharges or with narrow tubes some of the spark lines make their appearance. The tubes can only be run for a relatively short time, since the small amount of nitrogen is soon absorbed by the electrodes. The difficulty of admitting a further quantity of nitrogen has already been referred to, and arises from the want of control over the amount evolved when the alumina and

sodium azide mixture is heated. A marked excess leads to the appearance of the band spectra only, whilst a small excess causes confusion of the new lines with the superimposed negative bands, which are particularly strong under these conditions.

Similar experiments carried out with argon led to negative results, the new spectrum not appearing under any of the conditions employed. Merton and Pilley discuss these phenomena and offer the following interesting explanation, suggesting that the action of the helium is two-fold. In the first place, the expectation of life of a neutral nitrogen atom will become greater as the partial pressure of that gas decreases, and in helium at a high pressure, containing a very small trace of nitrogen, the conditions will be favourable to the passage of a heavy discharge, which could not be maintained at very low pressures, and also to the existence of a considerable proportion of the nitrogen in the atomic state. This effect is to be expected with any of the inert gases and indeed with the diatomic gases as diluents, but the latter case need not be considered, since at the necessary dilution the nitrogen lines would not be visible with any other diluent than an inert gas, and further complications would arise from the formation of compound molecules. It is evident that the greater the dilution the more favourable would be the conditions for the production of line spectra, since the presence of an excess of molecules would result in a preponderating emission of band spectra, with lower radiation potentials. At relatively high pressures the mean free path would be so small that unless the proportion of molecules were very small, there would be little chance of an electron ever requiring the energy required to excite the line spectra.

In the second place with condensed discharges through vacuum tubes the excitation must be very heterogeneous, and it may be supposed that forces varying over a wide range are available. As was pointed out above, an excess of nitrogen molecules may prevent the electrons from acquiring sufficient energy to excite the line spectra. The helium must act in precisely the same way; the first resonance potential of helium is 20·4 volts and a large excess of helium atoms in the vacuum tube must act as "safety valves" which blow off when they are struck by 20·4-volt electrons, and which therefore set a superior limit to the energy which there is any significant probability that an electron will acquire. If it be assumed that both in the case of nitrogen and carbon the energy required to excite the arc lines is less than 20·4 volts, and greater than this value for the excitation of the spark spectra, it may be understood how the presence of an excess of helium may result in the complete isolation of the arc spectrum.

The resonance potential of argon is 11·5 volts, and it is evidently possible for spectrum lines having radiation potentials between 11·5 and 20·4 volts to be suppressed by an excess of argon, though they may appear readily in the presence of helium, and Merton and Pilley suggest that the arc spectra of nitrogen and carbon belong to this category.

It is interesting to note that a preliminary analysis of the spectrum of the neutral nitrogen atom has been made by Kiess,[1] who finds that the spectrum is based on doublet and quartet terms as was to be expected. Moreover Fowler [2] has been able to show the analogy between this spectrum and that of singly-ionised oxygen, which is in accordance with the law of spectroscopic displacement, since the oxygen atom possesses one valency electron more than the nitrogen atom.

The spectra of carbon are of great importance from several points of view, both astrophysical and terrestrial, and they present considerable complexity, since in addition to the line spectra of elementary carbon there are several band spectra due to its compounds. For many years three band spectra have been known which are due to molecules containing carbon. These are the Ångström band spectrum, which has also been called the carbon oxide spectrum, the Swan spectrum, and the cyanogen or carbon nitride spectrum. The first of these makes its appearance during the filling of vacuum tubes if, as is nearly always the case, carbon dioxide is present during the preliminary exhaustion of the tubes. It consists of a series of bands, degraded towards the ultra-violet, the principal heads of which are at $\lambda = 6623, 6299, 6097, 5610, 5198, 4835, 4511$, and 4123. The Swan spectrum can be obtained under certain conditions in vacuum tubes and also can be seen in the inner blue cone of a roaring Bunsen burner. This spectrum consists of a series of band groups degraded towards the short wave-lengths, each band having a principal and several well-marked subsidiary heads. The wave-lengths of the principal heads are $\lambda = 6188, 5635, 5165, 4737$, and 4381. In addition to these there are certain bands attributed to a carbon-hydrogen complex.

The origin of the Ångström and Swan spectra has been the subject of much discussion, the general pre-Bohr view being that the Swan spectrum is due to elementary carbon, and that the Ångström bands are due to carbon monoxide, this view being based on the well-known fact that carbon dioxide is largely dissociated by electric sparks into the monoxide and oxygen. This opinion was adopted by Kayser in his *Handbuch der Spectroscopie*. Against this view I found in 1892 that if a vacuum tube is filled with absolutely pure carbon monoxide it gives the Swan spectrum and not the Ångström spectrum, the admixture of a trace of oxygen being sufficient to cause the change from the former to the latter. In order to obtain the Swan spectrum in this way, it is necessary to adopt rigid precautions against the presence of any oxygen. In the first place the vacuum tube must be very carefully cleaned and then after exhaustion it must be heated, the exhaustion being carried to the highest possible limit. The carbon monoxide must be prepared by the action of strong sulphuric acid on formic acid, both acids having previously been freed from dissolved air by being kept in a vacuum for some hours. The inverted syphon

[1] *Journ. Opt. Soc.*, America, **11**, 1 (1925).
[2] *Proc. Roy. Soc.*, A, **110**, 476 (1926).

and test tube shown in Fig. 54 on p. 163 may be used. The test tube is first thoroughly cleaned with hot chromic acid solution, washed, and dried. It is then filled with pure mercury, care being taken that no air bubbles are present. The test tube is then inverted over mercury in a trough and a few cubic centimetres of the strong sulphuric acid are introduced by means of a bent pipette, and then a few drops of the formic acid. The carbon monoxide thus formed can then be introduced through the inverted syphon into the vacuum tube. If these precautions are taken, the Swan spectrum is always obtained, the discharge having a brilliant green colour.

Smithells,[1] approaching the question from the side of combustion, also observed the spectra of the two oxides of carbon in vacuum tubes, and found that the Swan spectrum is given by carbon monoxide when it is absolutely pure. To this evidence it may be added that when vacuum tubes are filled with oxygen mixed with a trace of either oxide of carbon, the Ångström bands are always obtained.

It is true that the upholders of the alternative view had before them observations which at first sight seemed to be in favour of that view. For example, the Swan spectrum is shown by the carbon arc under liquids containing no oxygen,[2] and by the spark under liquids containing carbon and no oxygen.[3] It is highly probable, however, that these results were vitiated by the incomplete absence of dissolved oxygen in the liquids used.

The advent of the Bohr theory has of course disposed of any idea that the Swan spectrum can be due to the carbon atom, and in the present state of our knowledge it is not possible to discuss the existence of a gaseous molecule of carbon. It cannot be said therefore that the result of the Bohr theory has been a definite conclusion that the Swan spectrum is not due to elementary carbon. On the other hand, I am myself convinced that this spectrum is characteristic of carbon monoxide. More recent work has shown that the problem is much more complex than the foregoing would show, and it seems indeed that, like the nitrogen molecule, the two oxides of carbon can exhibit different band spectra under different conditions of excitation.

In dealing with the present state of knowledge of the many spectra of carbon, we may first consider the line spectra. It has been long known that in ordinary regions of investigation there is only one line in the arc spectrum of carbon which can definitely be assigned to that element, and that is the line at $\lambda = 2478$. On the other hand, it has also been known that a line spectrum is developed when a condensed discharge is passed through carbon monoxide in vacuum tubes. This spectrum has recently been investigated by Fowler,[4] who employed the spark between graphite poles in air and hydrogen, the arc in vacuo, and carbon compounds—chiefly carbon dioxide and hydrocarbons in vacuum tubes. He has succeeded in analysing the spectrum into series

[1] *Phil. Mag.*, **1**, 476 (1901). [2] Konen, *Ann. der Phys.*, **4**, 742 (1902).
[3] Watts and Wilkinson, *Phil. Mag.*, **12**, 581 (1906).
[4] *Proc. Roy. Soc.*, A, **105**, 299 (1924).

which are based on doublet terms, and this conforms with the law of spectroscopic displacement, since there is evidence that the spectrum of neutral boron is based on doublet terms [1] like the spectra of other elements of the third group. As will be shown below the arc spectrum of carbon has been observed by Merton and Johnson.[2] As will be shown in Vol. III., Chapter I., Millikan and Bowen have observed in the extreme ultra-violet the lines due to doubly- and trebly-ionised carbon atoms.

As regards the band spectra of carbon we are indebted to Fowler [3] for an important advance in this field, which, apart from its interest as regards the molecular origin of these spectra, has a great importance in connection with the spectra of comets. It has long been known that the heads or nuclei of comets exhibit the characteristic bands of carbon, and it was assumed that the spectra of the tails of the comets were similar. It was shown, however, by Deslandres and Bernard,[4] that this was certainly not true in the case of Daniel's comet (1907*d*) since the tail exhibited three bands of unknown origin. The head of this comet showed the yellow, green, and blue hydrocarbon bands and the ultra-violet cyanogen band at $\lambda = 3883$. The tail exhibited three bands with their centres at about $\lambda = 455$, 426, and 402, these bands not having been previously observed. It must be noted that Deslandres and Bernard employed a prismatic camera without a slit, so that wave-length measurements were of necessity only approximate. Chrétien [5] confirmed these observations and further found that each of the three bands had two heads.

The comet Morehouse (1908*c*) again showed these same bands when the spectrum of the tail was examined, and Fowler, realising that in all probability the density of gases in the tails of comets is very low, was convinced that the most promising field of investigation of the origin of the new spectrum lay in the spectra of high vacua. He succeeded in proving that a vacuum tube containing carbon monoxide at very low pressures exhibited the new bands. The pressure must be so low that the light from the discharge is only just visible. He also found that the spectrum was produced by the use of a hot lime cathode with carbon monoxide under very low pressures. These bands are now usually known as the comet tail spectrum. The essential characteristic of this spectrum is that the bands are degraded towards the red.

During this work Fowler discovered another spectrum given by carbon monoxide at higher pressures (100 mm.), and this is known as the high-pressure CO spectrum. It consists of six bands degraded towards the ultra-violet. These bands, six in number, appear to have been observed in two comets, namely Borelly's comet (1903)

[1] Fowler, *Report on Series in Spectra*, p. 155. Fleetway Press, London, 1922.
[2] *Proc. Roy. Soc.*, A, **103**, 383 (1923).
[3] Royal Astronomical Soc., *Monthly Notices*, **70**, 176 (1909); **70**, 484 (1910).
[4] *Comptes Rendus*, **145**, 445 (1907). [5] *Ibid.*, **145**, 549 (1907).

and Comet (1910*a*). Fowler draws attention to the fact that the Ångström bands have not been observed in the spectra of the comets.

The reality of the agreement between Fowler's new low-pressure bands of CO and the comet tail spectrum was confirmed by some more accurate observations on Comet Morehouse in 1911 by de la Baume Pluvinel and Baldet.[1]

The whole problem of the spectra associated with carbon was investigated by Merton and Johnson,[2] who studied the conditions for obtaining the various band spectra and made more accurate measurements of the wave-lengths of the heads than had previously been done. This investigation may be discussed in some detail.

Merton and Johnson do not concern themselves much with either the Swan spectrum or the Ångström bands, since these are sufficiently well known, but in passing they point out that the former is readily given by vacuum tubes containing carbon monoxide when a condenser and small spark gap is used and that its appearance is aided by the presence of helium, neon, or argon. They further draw attention to the fact that the Ångström bands are usually accompanied by a number of faint bands, degraded towards the red, and these bands will again be referred to below.

The hydrocarbon bands, which appear with the Swan spectrum in the blue cone at the base of the Bunsen or Meker flame, are also found in the spectrum of the discharge through vacuum tubes containing carbon and hydrogen. They are exhibited with great brilliance by vacuum tubes with carbon electrodes, provided with side tubes containing potassium hydroxide and phosphorus pentoxide, and with a palladium tube through which hydrogen is admitted to a pressure of a few millimetres. The bands appear together with the Swan bands when the vacuum tubes are excited by an uncondensed discharge. They form a complex system of bands with a principal head at $\lambda = 4315$ degraded towards the ultra-violet. It is interesting to note that Newall, Baxendall and Butler[3] have identified this band with the characteristic band in the solar spectrum known as G. They point out the importance of this band in the interpretation of stellar spectra.

Merton and Johnson succeeded in isolating the Fowler high-pressure CO bands almost completely from other spectra. Vacuum tubes were used with carbon electrodes and side tubes containing magnesite, phosphorus pentoxide, and a regulator of palladium for removal of hydrogen. Carbon dioxide was admitted into the vacuum tube by heating the magnesite, and at first the Ångström bands only were observed, no trace of the high-pressure bands being visible. After the uncondensed discharge is passed for some time, the carbon dioxide being presumably reduced to the monoxide, the high-pressure bands appear in the capillary portion of the vacuum tube.

With the condensed discharge at pressures over 5 mm. the bluish

[1] *Astrophys. Journ.*, **34**, 89 (1911). [2] *Proc. Roy. Soc.*, **103**, 383 (1923).
[3] Royal Astronomical Soc., *Monthly Notices*, **76**, 640 (1916).

jets seen at the ends of the capillary tube show the high-pressure bands with a trace only of the Swan spectrum. There are six bands in this spectrum, each with double heads degraded towards the violet, the wave-lengths being—

6441	5897	5431	5030	4679	4365
6420	5878	5413	5015	4663	4353

The influence of helium on the secondary spectrum of hydrogen has already been discussed (see p. 210), and it has now been found that the comet tail bands appear when a trace of a carbon compound is present in helium. Merton and Johnson succeeded in obtaining vacuum tubes which show nothing but the comet tail bands and somewhat feebly the principal helium lines. Vacuum tubes of the H-form are used with the central capillary portion replaced by a tube of about 20 mm. bore. The tubes are provided with carbon electrodes and side tubes containing phosphorus pentoxide and potassium hydroxide and also a palladium regulator. It is convenient to exhaust the tube by means of charcoal in a U-tube cooled in liquid air, after a preliminary evacuation by an oil pump, and to admit helium, obtained by heating thorianite, through the cooled U-tube until a pressure of 20 mm. is obtained. The spectrum at this stage shows the Ångström and Swan bands, together with the helium lines.

The discharge is now maintained through the tube for a considerable time, the palladium regulator being simultaneously heated. After some time the comet tail bands appear suddenly, and the whole tube glows with a greenish colour in which the helium lines are faintly visible. In Table XXXV. are given the wave-lengths of the heads of the bands as measured by Merton and Johnson. In this table, which is taken from their paper, the first column contains de la Baume Pluvinel and Baldet's measurements of the bands given by Comet Morehouse, which were made with a prismatic camera. The second column contains Fowler's measurements of the heads, and in the third column are given Merton and Johnson's values. The letters A, B, and C refer to the classification of the heads set up by Fowler. As can be seen each band has two double heads, and these are grouped as shown in Table XXXV. Fowler grouped the heads observed by him into two series, A and B, and he calculated the series C, none of which were observed by him but which agree fairly well with some of the comet bands. Merton and Johnson observed two of the C series, and, further, the relative intensities noted by them differed markedly from those given by Fowler. This would seem, therefore, to be a further example of the change in a spectrum caused by the admixture of helium.

The number of bands observed are insufficient to enable a complete calculation of the formulæ, but the wave-numbers given in the last column of Table XXXV. are those given by the formula—

$$\nu = \mathrm{K} - 13{\cdot}5\,(m + 0{\cdot}30)^2,$$

TABLE XXXV.

Comet-tail bands (Pluvinel and Baldet).	Low-pressure CO bands (Fowler).	Int.	Wave-lengths in I.A.	Int.	Series.	Wave-number in vacuo.	
						Obs.	Calc.
7027·4	—	—	—	—	—	—	—
6848·4	—	—	—	—	—	—	—
6254·5	—	—	6245·9 6239·1	10	57C	16006 16023	16007 16023
			6196·5 6190·0	7		16134 16150	16134 16150
6020	—	—	—	—	—	—	—
—	—	—	5699·1 5694·1	2	56C	17542 17557	17541 17556
—	—	—	5658·6 5653·0	0		17667 17685	17667 17683
5562	5510	2	5504·7 5500·3	10	57B	18161 18176	18161 18176
5482	5473	2	5466·8 5461·9	7		18287 18303	18287 18303
5259·8*d*	—	—	—	—	—	—	—
5106·7	5078	5	5075·9 5072·3	7	56B	19695 19709	19695 19710
5021·2	5049	5	5043·8 5039·7	5		19821 19837	19821 19837
4986·7	—	—	—	—	—	—	—
—	4916 ?	—	4914·0 4910·6	6	57A	20344 20358	20344 20359
—	4887 ?	—	4883·7 4880·0	3		20471 20486	20471 20487
4879·0	—	—	—	—	—	—	—
4846·1	—	—	—	—	—	—	—
4721·9	4715·0	3	—	0	55B	—	21201
			—			—	21216
4695·3	4688·5	3	4687·0 4684·3	1		21239 21341	21328 21343
4575·8	4570·5	5	4569·6 4566·2	7	56A	21877 21894	21877 21893
4549·2	4545·4	6	4542·9 4539·9	4		22006 22020	22004 22020
4522·7	—	—	—	—	—	—	—
4411·9*c*	—	—	—	—	—	—	—
4387·7*c*	—	—	—	—	—	—	—
4373	—	—	—	—	—	—	—
4279·0	4276·0	10	4274·3 4272·1	2	55A	23389 23401	23385 23400
4256·9	4253·2	8	4252·5 4249·1	0		23509 23528	23511 23528
4236·3	—	—	—	—	—	—	—
4143·7*c*	—	—	—	—	—	—	—
4114·0*c*	—	—	—	—	—	—	—
4023·3	4020·4	8	—	—	—	—	—
4003·4	4001·3	6	—	—	—	—	—
3990·6	—	—	—	—	—	—	—

c = confused with other bands.
d = unresolved pair. Wave-length at centre.

TABLE XXXV.—*Continued.*

Comet-tail bands (Pluvinel and Baldet).	Low-pressure CO bands (Fowler).	Int.	Wave-lengths in I.A.	Int.	Series.	Wave-number in vacuo.	
						Obs.	Calc.
3907·6	3907 ?	—	—	—	—	—	—
3898·2	3891 ?	—	—	—	—	—	—
3803·4	3797·6	6	—	—	—	—	—
3782·6	3781·0	6	—	—	—	—	—
3701	3707·5	3	—	—	—	—	—
3687	3693·0	3	—	—	—	—	—
3611	3602·0	3	—	—	—	—	—
3586	3587·0	2	—	—	—	—	—
3530	—	—	—	—	—	—	—
3519	—	—	—	—	—	—	—
3508	—	—	—	—	—	—	—
3446	3429·0	2	—	—	—	—	—
3436	3415·0	2	—	—	—	—	—
3385	—	—	—	—	—	—	—
3357	—	—	—	—	—	—	—
3294	—	—	—	—	—	—	—
3269	—	—	—	—	—	—	—

where K = A_{1234}, B_{1234}, C_{1234}, and

$A_1 = 64668$	$B_1 = 62458$	$C_1 = 60332$
$A_2 = 64683$	$B_2 = 62500$	$C_2 = 60347$
$A_3 = 64795$	$B_3 = 62611$	$C_3 = 60458$
$A_4 = 64810$	$B_4 = 62627$	$C_4 = 60474$

Fowler's formula for the more refrangible heads are

$$\text{A series: } \nu = 65008 - 13{\cdot}5\,(m + 0{\cdot}444)^2$$
$$\text{B series: } \nu = 62822 - 13{\cdot}5\,(m + 0{\cdot}444)^2$$
$$\text{C series: } \nu = 60663 - 13{\cdot}5\,(m + 0{\cdot}444)^2$$

Reference was made to the general appearance in the Ångström band spectrum of a number of faint bands degraded towards the red. Merton and Johnson succeeded in isolating these bands and in identifying them as a new band spectrum of carbon. The method of procedure is exactly the same as that given above for the production of the comet-tail spectrum, and when this spectrum has been obtained a small quantity of hydrogen is admitted through the palladium regulator. The comet-tail bands then disappear almost entirely, giving place to a spectrum consisting of triplet bands degraded towards the red, together with faint indications of the Swan and Ångström bands. The wave-lengths of the heads of the new bands, together with those of certain other heads which probably belong to some other system, are given in Table XXXVI. The most refrangible heads of these triplet bands are in reality double, so that there are in fact four heads to each band. In some cases the double head could not be resolved.

TABLE XXXVI.

Wave-lengths in I.A.	Intensity.	Series.	Wave-number, obs.	Wave-number, calc.
6464·6	10	57A	15465	15466
5433·1			15540	15539
6403·8			15611	15614
6399·0			15623	15623
6383·1	1		15662	
6348·7			15747	
—			—	
6319·8			15619	
6037·0	8	56A	16560	16557
6010·5			16633	16630
—			—	16704
5980·7			16716	16713
5836·9	2		17128	
5812·1			17201	
5780·9			17294	
5777·1			17305	
5670·5	6	55A	17630	17628
5647·6			17702	17701
5626·0 *c*			17770	17776
5621·7			17783	17785
5554·1	5	53B	18000	17998
5532·5			18070	18071
5509·7			18145	18146
5507·1			18153	18154
5428·3	1		18417	
5414·5			18464	
—			—	
5402·5			18505	
5351·3	5	54A	18682	18681
5330·5			18755	18754
5309·5			18829	18828
5307·2			18837	18837
5258·3	5	52B	19012	19012
5238·4			19085	19085
—			—	19160
5215·3			19169	19168
5140·3	2		19448	
5128·1			19495	
—			—	
5116·2			19540	

c = confused with other bands.

TABLE XXXVI.—*Continued.*

Wave-lengths in I.A.	Intensity.	Series.	Wave-number, obs.	Wave-number, calc.
5070·9	8	53A	19715	19715
5052·7			19786	19787
5033·8			19860	19861
5031·7			19868	19870
4996·9	6	51B	20007	20007
4979·0			20079	20080
4960·5			20154	20154
4958·2			20163	20163
4949·8	2		20197	
4935·5			20256	
4920·0			20319	
4917·1			20332	
4823·5	8	52A	20726	20728
4806·7			20798	20801
—			—	20875
4787·3			20882	20884
4764·8	5	50B	20981	20983
4747·5			21058	21056
—			—	21130
4729·1			21140	21139
4602·6	7	51A	21721	21723
4586·4			21797	21796
c 4572·2			21865	21870
4569·2			21879	21879
4556·8	5	49B	21939	21939
4541·3			22014	22013
4526·2			22087	22087
4524·7			22095	22096
4454·5	1		22443	
4445·5			22488	
4438·0			22526	
4436·4			22534	

c = confused with other bands.

The triplet bands consist of two distinct series, the wave-numbers being given by the formula—

$$\nu = K - 9{\cdot}5665\,(m + 0{\cdot}5)^2$$

where $K = A_{1234}$, B_{1234}, and

$A_1 = 47095$ $B_1 = 45380$
$A_2 = 47169$ $B_2 = 45453$
$A_3 = 47243$ $B_3 = 45527$
$A_4 = 47252$ $B_4 = 45536$

Yet another spectrum is obtained when the ordinary discharge through the vacuum tubes, prepared as already described for the comet-tail bands, is replaced by a condensed discharge using a small spark gap. A line spectrum is then obtained, which contains in addition to the lines of helium, some of the lines of oxygen and on occasion the Balmer lines, a number of new lines which have been assigned to carbon, since it has been found impossible to reproduce them in the absence of that element. Merton and Johnson in discussing this new spectrum suggest that it may perhaps be the true arc spectrum of carbon which the energy in the carbon arc is not sufficient to develop, and which the much greater intensity of condensed discharges under ordinary conditions is sufficient to suppress. It is not probable that it belongs to the class of enhanced spectra.

More recently the comet-tail spectrum has been studied by Baldet,[1]

TABLE XXXVII.

6354	6361	6405	6412
6189·35	6196·43	6238·72	6244·95
5970	5976	6015	6021
5856·51	5862·31	5900·40	5905·66
5764	5769	5806	5812
5652·60	5658·09	5693·59	5698·59
5461·42	5466·74	5499·86	5504·46
5389·25	5393·92	5426·44	5430·51
5281	5286	5317	5321
5209	5214	5244	5248
5039·77	5043·70	5072·06	5075·88
4879·51	4883·86	4910·96	4914·54
4836·58	4839·55	4865·83	4868·98
4683·37	4686·80	4711·25	4714·48
4664·54	4667·98	—	—
4539·38	4542·63	4565·83	4568·71
4517·99	4521·00	—	—
4378·93	4381·38	4403·26	4406·24
4248·55	4251·27	4271·31	4273·87
4244·10	4246·16	—	—
4130·39	4132·53	4151·92	4153·82
4117·28	4119·38	4138·92	4140·42
3997·21	3999·50	4017·60	4019·76
3888·55	3890·53	3908·00	3909·90
3777·61	3779·49	3795·65	3797·37
3688·09	3689·84	3705·31	3707·10
3584·11	3585·74	3600·74	3602·26
3510·27	3511·72	3525·64	3526·95
3413·29	3414·58	3427·85	3429·20
3351·71	3352·94	3366·02	3366·98
3300·66	3302·06	3314·18	3315·50
3260·35	3261·58	3273·91	3275·24
3209·64	3210·67	3222·42	3223·47
3168·03	3169·07	3180·26	3181·34
3123·18	3124·47	3135·51	3136·77
3081·46	3082·71	3093·30	3094·57

[1] *Comptes Rendus*, **178**, 1525 (1924); **180**, 271, 820, 1201 (1925).

who succeeded in exciting these bands by the action of the thermionic discharge on carbon monoxide at low pressures. It will be remembered that Fowler found a lime cathode in his experiments very satisfactory. Baldet employed a tungsten cathode and he also maintained a slow stream of carbon monoxide through the vacuum tube, the pressure being kept constant by means of a Holweck pump backed by an oil pump. At very low pressures the comet-tail bands are developed with considerable intensity, and they were photographed through a quartz window with a spectrograph of high dispersion.

The complete list of the wave-lengths of the heads of these bands are given in Table XXXVII.

There have thus been measured thirty-six bands, each with four heads, though in three cases the less refrangible double heads could not be measured owing to the overlapping by other lines.

Baldet states that in his tubes when the pressure of the carbon monoxide is about 0·7 mm. three new carbon bands are developed with considerable intensity. These bands, like the comet-tail bands, each have two double heads, but they are degraded towards the violet. His measurements of the heads are given in Table XXXVIII.

TABLE XXXVIII.

4236·46	4231·01	4213·06	4208·71
3977·91	3973·17	3957·11	3953·32
3729·60	3724·76	3711·03	3707·12

It is difficult to attribute these bands with any certainty to the carbon monoxide molecule owing to the action of the electron stream from the hot cathode in causing the partial dissociation of a gas. There remains, however, the fact that the spectrum is given with considerable intensity by CO.

The following views expressed by Baldet would seem to be of some interest. When the pressure of the carbon monoxide in the vacuum tubes with an incandescent cathode is varied, the spectrum changes. The tungsten cathode emits a very large number of electrons which partake of the nature of a gas in the tube and which ionise the molecules. The luminescence is due partly to the collisions of neutral and ionised molecules with electrons which are travelling with a velocity greater than that corresponding to the ionisation potential, and partly to the collisions of the ionised molecules with one another and with neutral molecules. These different kinds of collisions give rise to different band spectra. At extremely low pressures when the electron collisions predominate, we have the comet-tail spectrum strongly developed and so it may be concluded that this spectrum has its origin in the collisions of the electrons with the carbon monoxide molecules.

The variation of pressure also introduces changes in the inner

structure of the comet-tail spectrum. At very low pressures the heads are intense and the series of lines originating in those heads are very short. As the pressure increases the line series increase considerably in length. The appearance of this CO spectrum at very low pressures resembles the spectrum of the comet tail quite closely, for the latter shows the band heads very rapidly degraded.

Baldet considers that these experimental results give material support to the view put forward by Deslandres in 1895, which, in modern language, states that the solar corona and the luminescence of comets are due to electron streams emitted from the sun.

The Spectra of Isotopes.—One of the most interesting problems arises in connection with the existence of isotopes and that is the question of the identity of their spectra. This question has been investigated more particularly in the case of the isotopes of lead. It was found in the first instance by Richards and Lembert [1] that there were only negligible differences between the spectra of ordinary lead and lead from radioactive sources. The matter has been investigated with great care by Merton, who first of all found that the lines are identical in the spectra of ordinary lead and lead in Joiachimsthal pitchblende,[2] and thus confirmed the previous observations. In a later paper [3] he described some very accurate measurements of the wave-length of the line $\lambda = 4058$ in the spectra of ordinary lead, lead from pitchblende, and lead from thorite. The method employed was to alloy the lead with cadmium and to compare the wave-lengths by interference methods with those of the cadmium lines $\lambda = 5086$ and 4800. In this first series of measurements Merton found the following wave-length differences :—

λ (lead from pitchblende) — λ (ordinary lead) = 0·0050A. ± 0·0007A.
λ (ordinary lead) — λ (lead from thorite) = 0·0022Å. ± 0·0008Å.

The former difference agrees fairly well with that found by Aronberg who compared ordinary lead with lead from Australian carnotite and obtained for the 4058 line a difference of 0·0044A. The three values obtained by Merton with the three samples of lead are in the order of their atomic weights. The reality of the difference was confirmed in the case of the thallium line $\lambda = 5350$, the wave-length difference being—

λ (ordinary thallium) — λ (thallium from pitchblende)
= 0·0055A. ± 0·0010A.

In a third paper Merton [4] compares a sample of lead from Australian carnotite with ordinary lead, and his final value for the wave-length difference of the 4058 line is—

λ (lead from carnotite) — λ (ordinary lead) = 0·011A. ± 0·0008A.

[1] *J. Amer. Chem. Soc.*, **36**, 1329 (1914).
[2] *Proc. Roy. Soc.*, A, **91**, 198 (1915).
[3] *Ibid.*, **96**, 388 (1920).
[4] *Ibid.*, **100**, 84 (1922).

This value is rather more than twice as great as that found previously with the lead from pitchblende, and the explanation is doubtless to be found in the greater purity of the uranium lead as obtained from the carnotite. Four other lead lines, $\lambda = 3740$, 3684, 3640, and 3573 were compared with the 4058 line in the spectra of the two types of lead, and the results obtained are given in Table XXXIX.

TABLE XXXIX.

	λ (carnotite lead) − λ (ordinary lead).	Wave-number (ordinary lead) − wave-number (carnotite lead).
3740	0·0074 ± 0·0011	0·053 ± 0·008
3684	0·0048 ± 0·0007	0·035 ± 0·005
3640	0·0070 ± 0·0003	0·052 ± 0·002
3573	0·0048 ± 0·0005	0·037 ± 0·004

In order to obtain the absolute values of the differences, the value obtained for $\lambda = 4058$ must be added to those for the other lines. The differences are evidently not the same for the different lines, though they appear to be almost identical for the lines $\lambda = 3740$ and 3640, and for the lines $\lambda = 3684$ and 3573. This is somewhat surprising for the lines $\lambda = 3740$ and 3573 apparently belong to the same series group.

From the Bohr theory it may be shown that the relation between the wave-lengths of the same spectrum line as given by two isotopes should be—

$$\frac{\lambda_2}{\lambda_1} = \frac{M_1(M_2 + m)}{M_2(M_1 + m)}$$

where M_1 and M_2 are the masses of the atoms of the two isotopes and m is the mass of an electron. From this we have—

$$\frac{\Delta\lambda}{\lambda_1} = \frac{m(M_2 - M_1)}{M_2(M_1 + m)},$$

and if we apply this to the lead line at $\lambda = 4058$ and take the atomic masses of ordinary and carnotite lead to be 207 and 208 the value is found of $\Delta\lambda = 0{\cdot}000047$. The difference of 0·011 finally found by Merton is therefore more than 200 times larger than that calculated on the simple Bohr theory. No satisfactory explanation of this very great discrepancy has as yet been found.

McLennan and Ainslie[1] investigated the red line of lithium at $\lambda = 6708$ and found that it consisted of a quartet with separations of 0·128A., 0·173A., and 0·165A. It may of course be suggested that as lithium consists of a mixture of two isotopes with atomic masses of

[1] *Proc. Roy. Soc.*, A, **101**, 342 (1922).

6 and 7, respectively, each of these gives a doublet. In the later paper McLennan, Ainslie, and Gale,[1] using Aronberg's value of 0·0044 for the separation for the lead line and the separation of the two lithium doublets, suggest that the observed separation is equal to the theoretical value multiplied by the atomic number of the element. Thus the atomic number of lithium is 3 and the theoretical separation is $\Delta\lambda = 0{\cdot}08$ and

$$0{\cdot}08 \times 3 = 0{\cdot}24,$$

which is of the same order as that observed. In the case of lead we have—

$$0{\cdot}000047 \times 82 = 0{\cdot}0385$$

which again is not greatly different from Aronberg's value. McLennan, Ainslie, and Gale apply this to the case of mercury and suggest that some of the observed components are due to the presence of five isotopes with atomic masses of 197, 198, 200, 202, 204, respectively. The atomic number of mercury is 80 and if the central component be attributed to the 200 isotope the calculated separations together with their products into 80 are given in Table XL.

TABLE XL.

Isotope.	Δλ.	Δλ × 80.	Δλ observed.
204	− 0·000268	− 0·02144	− 0·0210
202	− 0·000135	− 0·01080	− 0·0087
200	0·000000	0·00000	0·0000
198	+ 0·000138	+ 0·01104	+ 0·0086
197	+ 0·000279	+ 0·02032	+ 0·0182

In the last column are given the means of the values observed by Janicki and by Nagaoka.

This somewhat attractive suggestion would, however, seem to be effectively disposed of by Merton's latest value for the lead line, namely, 0·011. Further, it will be remembered that Nagaoka noticed variations in the relative intensities of the satellites of some of the bismuth lines caused by alterations in the conditions of excitation. The same phenomenon has been observed with the mercury line $\lambda = 5460$ by Meissner, which could not possibly be true if the satellites were due to different isotopes.[2]

The problem of the discrepancy between calculated and observed differences has been discussed by Ehrenfest,[3] who points out that Bohr only applied the formula given above to cases in which a single

[1] *Proc. Roy. Soc.*, A, **102**, 33 (1923).
[2] Private communication to Professor Sommerfeld. *Atombau und Spektrallinien*, 4te Auflage, p. 172, Vieweg, Braunschweig, 1924.
[3] *Nature*, **109**, 745 (1922).

electron only moves round the nucleus, that is to say, the hydrogen and ionised helium atoms. No investigations have as yet been made of the formulæ which satisfy the cases where several electrons are moving round the nucleus. Bohr holds the view that the electron responsible for the emission of a spectral series, although it remains outside the configuration of the inner electrons during the greater part of its orbit, penetrates in certain cases into the interior of the atom during its revolution. A penetration of the electron deeply into the atom for a part of its orbit may very possibly be of great importance, since the effect of the mass of the nucleus might differ essentially from that calculated from an examination of the mechanical properties of the motion in the outer portion only of the orbit.

CHAPTER IV.

FLUORESCENCE AND PHOSPHORESCENCE.

It is a well-known fact that many substances, when submitted to the influence of light or cathode rays, develop the power of emitting luminescence in the visible or ultra-violet region of the spectrum, which has no connection with ordinary thermal radiation. This luminescence is observed with substances in each of the three states of gas, liquid, and solid, and in general the wave-lengths of the luminescence are characteristic of the chemical composition of the excited material. Closely associated with this phenomenon are two more manifestations of the radiation of energy of characteristic wave-lengths by solid substances, namely, thermoluminescence and triboluminescence. By the former is meant the development of a characteristic emission of light when certain solid materials are heated, whilst the latter includes the cases when the characteristic emission of light is caused by mechanical disturbance of the solid mass, such as powdering or rubbing in a mortar. In this chapter this whole group of associated phenomena will be discussed, together with an attempt to find an explanation of them. It is incumbent on us first to clear the ground by an explanation as to what exactly is meant by the two principal terms, fluorescence and phosphorescence, and this is rendered all the more necessary by the fact that considerable confusion has, at times, arisen from an insufficient understanding of their meaning. The original differentiation between the two terms was based on the fact that the phenomenon of luminescence emission was found to be of two types. In the one the luminescence is only visible during the period of excitation and vanishes the instant the excitation ceases, whilst in the other the luminescence continues for a measurable time after the excitation has ceased. It was therefore believed, and rightly so, that two different phenomena exist, and the name of fluorescence was given to the vanishing type of luminescence, and the name of phosphorescence was used in describing that type of luminescence which continues for a finite period after the excitation has ceased. This continuance of luminescence after the cessation of the excitation is known as persistence, and phosphorescence is said to persist for a certain period of time. This persistence varies enormously with different substances; with some it is very short, and with others it is very long indeed. By the use of suitable apparatus it is perfectly possible

to measure this persistence and to determine the length of time taken for the phosphorescence to decline to the point at which the intensity is too small to measure. In some cases the persistence is so short that the whole of the intensity vanishes in a small fraction of a second, and consequently it is not surprising that the question was asked as to whether the persistence could be taken as a sound method of differentiating between the phenomena of fluorescence and phosphorescence. It was considered that by the steady advance in phosphoroscopic technique more and more cases which had been believed to be fluorescence might be found to be phosphorescence, and in view of the uncertainty thus caused in the minds of those interested it was thought advisable to group the whole phenomena under the single name of phosphorescence. This was unfortunate, and some confusion was inevitable, since it seemed that only one phenomenon existed. Far better was the alternative designation of luminescence, which was adopted by many, especially in America. The difficulty was accentuated as our knowledge was extended. As a general rule, in the cases of indubitable fluorescence the emission of light takes place at wave-lengths which are shorter than those of the emission which is undoubtedly phosphorescence. When it was found that in certain cases evidence existed of the simultaneous excitation of fluorescence and phosphorescence at the same wave-lengths, and of the apparent change of the fluorescence into phosphorescence and *vice versa*, at those same wave-lengths, the difficulties of differentiating between the two were greatly enhanced. In the absence of any theoretical explanation of the whole series of phenomena and of these last observations in particular, it became increasingly evident that it was advisable to group all the luminescence phenomena together under one name. It seems probable, however, that the two phenomena of fluorescence and phosphorescence are entirely distinct from one another, this view being rendered more conclusive when the modern theories of the absorption and radiation are applied. In the present chapter these names will be used, and in the concluding section the reasons for this will be given.

There is no question but that the whole group of luminescence phenomena with which we are at the present moment concerned is due to the absorption of energy and its radiation, both taking place at frequencies which are characteristic of the substance under investigation. The first point which arises, therefore, is the phenomenon of absorption, that is to say, what actually takes place when energy is absorbed. As will be shown later, the luminescence phenomena are stimulated by light of definite wave-length, cathode rays, and sometimes by X-rays. Little can be said as regards the wave-lengths at which excitation takes place in the last two cases, but when the absorption of light energy is the cause of the luminescence it is possible to gain complete information of the wave-lengths. When molecules are exposed to radiant energy of a frequency which they are capable of absorbing, one of two phenomena may occur. In the one case the

energy is absorbed and radiated again in another region of the spectrum, the phenomena of fluorescence and phosphorescence being special instances of this case. In the other case the molecules become a source of energy of the same frequency as that which they absorb, this phenomenon being known as optical resonance. Up to the present this resonance has only been observed with gases, no evidence of it having been found with liquid or solid substances or with solutions. Within the strict meaning of the word, this phenomenon is one of luminescence, and consequently it may well fall within the purview of this chapter. This optical resonance may be discussed first, but before taking it up we may consider in a general way the phenomena of fluorescence and phosphorescence. The essential feature of these two manifestations of the radiation of definite frequencies is that these frequencies are smaller than those which, in being absorbed, stimulate them. The phenomenon of fluorescence is a familiar one to organic chemists, since many of their own group of compounds luminesce when exposed to light, the phenomenon being especially noticeable when the particular compounds are in solution in a colourless solvent. One of the examples best known to the ordinary man is the bright blue fluorescence of a solution of the bisulphate of quinine. The phenomenon of phosphorescence, on the other hand, is familiar from the old-fashioned luminous paints which contained impure barium or calcium sulphide, and were activated by exposure to sunlight, and thereby rendered visible in the dark, owing to the persistence of the phosphorescence for a long period after the excitation by light had ceased.

It must clearly be understood at the outset that whilst all substances absorb light at their characteristic frequencies, fluorescence or phosphorescence by no means always makes its appearance. When either one or both appear it means that some condition exists which is necessary, but as far as our knowledge goes at present it is not possible to define that condition.

One of the earliest observations of these luminescence phenomena is that made by Sir David Brewster,[1] who noted the fluorescence of chlorophyll, which is the green pigment present in the leaves of living plants. A very important study of the whole subject was made by Sir George Gabriel Stokes,[2] who was the first to enunciate the principle that fluorescence and phosphorescence always occur at wave-lengths which are longer than those which excite them. This is known as Stokes' law, and has been confirmed in very convincing fashion by numerous observations. Statements have been made on occasions to the effect that cases exist in which this law is disobeyed, but, as will be shown subsequently, these divergences from the law are unreal. In historical sequence we next must refer to the brilliant work by E. Becquerel [3] on phosphorescence, in the course of which he devised

[1] *Trans. Roy. Soc.*, Edinburgh, **12** (1833).
[2] *Phil. Trans.*, **142**, ii. 463 (1852); **143**, i. 385 (1853).
[3] *Ann. Chim. Phys.*, **55**, 5 (1859); **62**, 1 (1861).

a phosphoroscope and measured the persistence and rate of decay of the intensity of the phosphorescent emission. From the spectacular point of view, the work of Crookes takes very high place, for he was one of the first, in 1878, to demonstrate the remarkably brilliant luminescence exhibited by many minerals and other substances under the influence of cathode rays. It will be remembered that he was a pioneer in the field of high vacua, and that this work on phosphorescence formed part of his long series of investigations.

Crookes found that certain minerals, when subjected to cathode streams in a vacuum tube, glowed with extraordinary brilliance. For example, specimens of diamond were found which glowed with each of the colours bright blue, pale blue, apricot, red, yellowish-green, orange, and light green. Again, alumina in its various forms was found to be strikingly luminescent, in nearly all cases glowing with a rich full red, the spectrum showing a faint, continuous light, ending in the red near the B line, after which comes a black space and then a very brilliant and sharp red line. Emeralds luminesce with a crimson colour, sapphires with a bluish-grey, and certain specimens of tinstone were found which glowed with a yellow light. Spodumene also has a golden yellow luminescence under the same conditions, but shows no distinctive spectrum lines. Glucina, when prepared with special care, was found to luminesce with a continuous spectrum, showing a bright blue colour. Besides these natural minerals, certain artificially-prepared sulphides and sulphates were found to glow in a vacuum tube under the action of the cathode streams, with light giving either a continuous or a discontinuous spectrum. The latter is especially noticeable in the sulphates of the rare earth elements.

In addition to the above-mentioned substances, the following minerals give very characteristic colours under the influence of cathode rays. Lepidolite gives a deep crimson, willemite a magnificent green, calcite a red, strontianite a blue colour respectively. Again, it has been shown by Jackson that it is possible to prepare samples of lime which glow with different colours. A very beautiful effect can be produced by carefully calcining a sea-shell, such as a cockle-shell, and exposing it to the cathode rays. The lime thus produced glows with a variety of colours. This early work of Crookes forms an introduction to his later work on the phosphorescence of the rare earths, which, in the hands of Urbain and others, has proved so valuable an adjunct to the technique of the chemistry of these elements. This later development need not, however, be considered for the present, and we may now take up the first branch of our subject, namely, optical resonance.

Resonance Radiation and Resonance Spectra.

As already stated, the phenomenon of optical resonance has only been observed with substances in the state of vapour, and investigations of it have been made with the vapours of mercury, sodium, and iodine. The results obtained with the first two may be described.

The resonance spectrum of mercury vapour was first fully investigated by R. W. Wood, who published a summary of his experimental results in 1914.[1] It is well known that mercury vapour both emits and absorbs radiation of wave-length 2536 A., that is to say, this characteristic spectrum line is seen in the emission and absorption spectra of mercury vapour. The vapour pressure of mercury at ordinary temperatures is about 0·001 mm., and Wood showed that if a beam of monochromatic light of wave-length 2536, obtained by isolating the corresponding emission line of the quartz mercury lamp by means of a quartz monochromator, was focussed at the centre of a quartz bulb containing a drop of mercury vapour at ordinary temperature, the light was powerfully scattered by the vapour. In spite of this effect a considerable portion of the energy passes through the bulb without being influenced by the vapour. This is due to the fact that the density of the mercury vapour in the lamp is much greater than in the quartz bulb, with the result that the emission line has a finite breadth and that its central portion only is scattered by the cold vapour in the bulb. The path of the cone of light through the quartz bulb is readily traced by means of photography.

This phenomenon is true optical resonance, and Wood has also shown that the mercury vapour surrounding the exciting cone of light also emits light of wave-length 2536. This is due to a secondary scattering of the light emitted by the directly excited molecules, that is to say, the luminous cone of vapour acts as a source of radiation of $\lambda = 2536$, which stimulates the vapour which is not traversed by the incident beam.

Wood also investigated the resonance of sodium vapour when illuminated by light of the same wave-length as the D lines. Exactly the same phenomena were noticed as in the case of mercury vapour. In this investigation he was able to add the refinement of using only the D_2 line as the exciting radiation, when he found that only the D_2 line was emitted, no trace of the D_1 line being present in the scattered light. This establishes in the most definite way possible the absolute nature of the phenomenon of optical resonance. It must be noted, however, that this is only true in the complete absence of hydrogen.[2]

The optical resonance of sodium vapour has also been investigated by Lord Rayleigh,[3] who succeeded in observing the phenomenon with the line pair at $\lambda = 3303$, which is the second member of the principal series, the first member being the D lines. He also noted that under the stimulation by radiation of wave-length 3303 the D lines were emitted, which, in accordance with our definition, is a phenomenon of fluorescence, since the emission is at a different wave-length from that of the exciting radiation. In spite of this, however, the phenomenon cannot be grouped along with that of true fluorescence,

[1] *Proc. Phys. Soc.*, **24**, 185 (1914).
[2] Wood and Dunoyer, *Phil. Mag.*, **37**, 456 (1919).
[3] R. J. Strutt, *Proc. Roy. Soc.*, A, **91**, 388, 511 (1915); **96**, 272 (1919).

since it is merely the emission of a doublet of the principal series during the excitation of the atom by radiation of the next doublet in that series.

These results established the reality of optical resonance. There exists also a second phenomenon which was discovered by R. W. Wood [1] in his investigation of the optical properties of sodium vapour. It is well known that the normal absorption spectrum of sodium vapour consists of the principal series of doublets, the first members of which are the D lines and the pair at $\lambda = 3303$ to which reference has already been made. When the vapour is excited by white light or by certain monochromatic radiations which have not the same wave-lengths as the known absorption lines there are emitted banded spectra which are characterised by constant wave-length differences between the consecutive bands. The phenomenon lies, as it were, half-way between true fluorescence and true optical resonance, and the name of fluorescence spectra has been applied to it, though Wood himself prefers to call these spectra resonance spectra, the true optical resonance being called by him resonance radiation.

The resonance spectrum of sodium vapour excited by white light consists of a region in the orange-red and another in the greenish-blue, with a broad double band in the position of the D lines. The red and orange lines of lithium excite the red resonance spectrum, and are the only monochromatic sources which do so. The greenish-blue resonance, on the other hand, is excited by the radiations from several metallic arcs, and when it was found possible to isolate the single exciting line by means of a monochromator, the resonance spectrum was comparatively simple, consisting of widely separated lines, most of which were spaced at intervals of 38 A. In his earlier work Wood used a prism spectrograph for the observation of the resonance spectrum and the wave-lengths were only accurate to within about 2 A., but in his later work he employed a grating of 12-foot focus.

In the case of the excitation by the silver arc, the line at $\lambda = 5209{\cdot}6$ alone is active, and with the grating apparatus six lines were measured in the resonance spectrum. The wave-lengths of these can be expressed by the general formula $\lambda = \lambda_0 \pm mk$, where λ_0 is the wave-length of the exciting line, k is a constant, and $m = 0, 1, 2$, etc., as may be seen from Table XLI.

The mean value of k is 38·2 A., as determined from these six lines. In the earlier work with the prism apparatus nine additional lines were observed, and five of these appear to belong to the same series as those in Table XLI., the remaining four forming part of another series with the same constant wave-number difference.

In the case of the lead arc the resonance spectrum is excited by the line $\lambda = 5006{\cdot}1$, and contains a series of doublets as well as certain other lines, four of which can be apportioned to a series similar to the doublet series. This spectrum is shown in Table XLII.

[1] Wood and Moore, *Astrophys. Journ.*, **18**, 94 (1903); Wood, *Phil. Mag.*, **12**, 499 (1906); Wood and Hackett, *Astrophys. Journ.*, **30**, 339 (1909).

TABLE XLI.

			m	5209·6	*m* × 38·2
5133		76·6 = 38·3 × 2	2	5133·2	
	38·2				
5171·2		38·4 = 38·4 × 1	1	5171·4	
	38·4				
5209·6		exciting line	0	5209·6	
	38·3				
5247·9		38·3 = 38·3 × 1	1	5247·8	
	37·8				
5285·7		76·1 = 38·05 × 2	2	5286·0	
	37·7				
5323·4		113·8 = 37·9 × 3	3	5324·2	

TABLE XLII.

Intensity.	Wave-length.	Series A, $k = 39$.	Series B, $k = 39$.	Series C, $k = 37{\cdot}5$.
1	5372·2	—	—	—
1	5365·5	—	—	—
1	5337·3	—	—	—
1	5309·7*c*	—	—	113·3 = 3 × 37·8
3	5300·4	—	—	—
2	5278·8*a*	272·3 = 7 × 38·9	—	—
3	5272·1*c*	—	—	75·7 = 2 × 37·8
1	5266·9	—	—	—
2	5240·4*a*	233·9 = 6 × 39·0	—	—
2	5233·4*c*	—	—	37·0 = 1 × 37·0
1	5226·3	—	—	—
6	5202·4*a*	195·9 = 5 × 39·2	—	—
2	5196·4	—	—	—
4	5162·4*a*	155·9 = 4 × 39·0	—	—
4	5158·5*b*	—	194·1 = 5 × 38·8	—
4	5123·7*a*	117·2 = 3 × 39·1	—	—
4	5121·0*b*	—	156·6 = 4 × 39·2	—
6	5084·2*a*	77·7 = 2 × 38·9	—	—
6	6081·5*b*	—	117·1 = 3 × 39·0	—
2	5049·7	—	—	—
8	5045·2*a*	38·7 = 1 × 38·7	—	—
2	5042·4*b*	—	78·0 = 2 × 39·0	—
10	5006·5*a*	—	—	—
2	5003·4*b*	—	39 = 1 × 39·0	—
2	4967·5*a*	39·0 = 1 × 39·0	—	—
1	4964·4*b*	—	—	—
2	4929·4*a*	77·1 = 2 × 38·5	—	—

The barium line at $\lambda = 4934$ excites a remarkable series of equally-spaced lines, which are given in Table XLIII. At each end of this resonance spectrum there occur some lines which do not seem to belong to any series; these are included in the list, since their general appearance and intensity are the same as the series lines.

TABLE XLIII.

Intensity.	Wave-length.	Series A, $k = 38{\cdot}8$.	Series B, $k = 38{\cdot}4$.
1	5443·3	—	—
1	5425·3	—	—
1	5354·3	—	—
1	5341·1	—	—
1	5339·5	—	—
1	5336·6	—	—
1	5331·8	—	—
1	5321·3*a*	387·1 = 10 × 38·7	—
1	5318·5*b*	—	195·1 = 5 × 39·0
2	5303·6*c*	—	—
1	5300·2	—	—
1	5294·6	—	—
1	5291·3	—	—
2	5286·5*a*	352·3 = 9 × 39·1	—
2	5277·6*b*	—	154·2 = 4 × 38·5
1	5274·3	—	—
1	5267·4*c*	—	—
4	5245·9*a*	311·7 = 8 × 38·9	—
2	5241·2	—	—
1	5238·3*b*	—	114·9 = 3 × 38·3
8	5207·2*a*	273·0 = 7 × 39·0	—
2	5202·6	—	—
8	5200·0*b*	—	76·6 = 2 × 38·3
1	5198·2	—	—
1	5193·8	—	—
2	5192·6*c*	—	—
6	5167·7*a*	233·5 = 6 × 38·9	—
3	5164·2	—	—
6	5161·6*b*	—	38·2 = 1 × 38·2
8	5128·5*a*	194·3 = 5 × 38·8	—
2	5123·4*b*	—	—
1	5091·1	—	—
8	5089·1*a*	154·9 = 4 × 38·7	—
1	5088·7	—	—
1	5085·5	—	—
8	5050·3*a*	116·1 = 3 × 38·7	—
1	5046·9	—	—
6	5011·8*a*	77·6 = 2 × 38·8	—
4	5009·9	—	—
2	5007·1	—	—
6	4972·8*a*	38·6 = 1 × 38·6	—
1	4937·4	—	—
1	4935·7	—	—
10	4934·2*a*	—	—
2	4900·5*x*	—	—
4	4896·8*a*	37·4 = 1 × 37·4	—
2	4863·0	—	—
4	4860·9*a*	73·3 = 2 × 36·7	—
2	4761·2*x*	—	—
2	4756·8*x*	—	—
6	4726·5*x*	—	—
6	4691·5*x*	—	—
2	4673·8*x*	—	—
4	4606·9*x*	—	—
6	4599·2*x*	—	—
6	4580·3*x*	—	—
6	4574·6*x*	—	—
6	4562·1*x*	—	—
10	4554·0*x*	—	—

There are four lines in the lithium arc spectrum which excite resonance spectra of sodium vapour, namely, the lines at $\lambda = 6708$, 6104, 4972, and 4603. The spectrum excited by the 4972 line is interesting, since its principal series almost coincides with the principal series excited by the barium line at $\lambda = 4934$, the average distance between the corresponding lines being only 0·5 A. Wood was not successful in measuring the lines of the resonance spectrum excited by the line $\lambda = 4603$. The orange-red spectrum will be described below.

The resonance spectrum excited by the magnesium arc is due to the well-known green triplet, and it was not found possible to study the effect of these lines separately. The spectrum, therefore, consists of three series, one for each exciting line, and these are shown in Table XLIV., together with some other lines, indicated by *d*, *e*, *f*, *g* which seem to belong to secondary series of the same type.

A similar arrangement was observed with the resonance spectrum excited by the three copper lines at $\lambda = 5218$, 5153, and 5106.

Another phenomenon which was observed by Wood in connection with sodium vapour is the magnetic rotation spectrum. When plane polarised light is passed through sodium vapour in a magnetic field along the lines of force, a nicol prism, set to extinction in the absence of the field, transmits a brilliant orange-yellow light. The spectroscope shows that this light consists of a great number of bright lines in the greenish-blue and red with a narrow region of continuous spectrum near the D lines.[1] The lines in the green and red form the magnetic rotation spectrum, and they form narrow regions, possibly less than 0·1 A. in width, in which the plane of polarisation has been rotated through different angles, enabling the light to pass through the nicol prism. In the greenish-blue region 128 lines have been measured; whilst over 340 lines have been measured in the orange and red region.

Reference has already been made to the resonance spectrum of sodium vapour when excited by white light. This spectrum also consists of a region in the greenish-blue and another in the orange-red, together with a broad double band in the position of the D lines. There is a very interesting connection between the resonance and magnetic rotation spectra in the greenish-blue. The resonance spectrum extends from $\lambda = 5500$ to $\lambda = 4700$, the brightest portion being from $\lambda = 5500$ to $\lambda = 5000$. The latter contains a well-defined system of bands, each of which consists of a great number of fine lines. On the violet side of each band there is a narrow region, about 2 A. in width, where the intensity is zero. The lines of the magnetic rotation spectrum have the same wave-lengths as these dark spaces, with the result that the former are situated about 1 A. on the violet side of the resonance spectrum lines. In Table XLV. are given first the complete set of lines in the white light resonance spectrum, and then

[1] *Phil. Mag.*, **10**, 408 (1905); **14**, 145 (1907); **15**, 274 (1908); **18**, 530 (1909).

TABLE XLIV.

Intensity.	Wave-length.	Series A, $k = 38{\cdot}9$.	Series B, $k = 38{\cdot}1$.	Series C, $k = 38{\cdot}5$.
				—
1	5305·7	—	—	117·0 = 3 × 39·0
1	5300·8*c*	—	—	—
1	5298·2*e*	—	—	78·5 = 2 × 39·2
4	5262·3*c*	—	—	—
4	5257·1*d*	—	76·3 = 2 × 38·1	—
2	5249·2*b*	—	—	—
2	5245·0*a*	77·5 = 2 × 38·7	—	39·1 = 1 × 39·1
8	5222·9*c*	—	—	—
2	5220·4*e*	—	38·0 = 1 × 38·0	—
8	5210·9*b*	—	—	—
10	5183·8*c*	—	—	—
1	5180·9*e*	—	—	—
10	5172·9*b*	—	—	—
10	5167·5*a*	—	—	38·7 = 1 × 38·7
6	5145·1*c*	—	—	—
2	5142·4*e*	—	—	—
2	5139·8	—	—	—
6	5135·0*b*	—	37·9 = 1 × 37·9	—
2	5133·7*g*	—	—	—
2	5128·3*a*	39·2 = 1 × 39·2	—	—
2	5124·5	—	—	—
1	5110·8*g*	—	—	—
6	5106·6*c*	—	—	77·2 = 2 × 38·6
1	5101·5*d*	—	—	—
4	5097·3*b*	—	75·6 = 2 × 37·8	—
4	5094·9*g*	—	—	—
2	5088·9*a*	78·6 = 2 × 39·2	—	—
2	5059·6*b*	—	113·3 = 3 × 37·8	—
2	5055·4*g*	—	—	—
2	5050·0*a*	117·5 = 3 × 39·0	—	—
2	5034·1	—	—	—
4	5030·2*c*	—	—	153·6 = 4 × 38·4
2	5022·7*f*	—	—	—
Missing	5019·5	—	—	—
4	4991·9*c*	—	—	191·9 = 5 × 38·4
4	4984·5*f*	—	—	—
4	4979·7*b*	—	193·2 = 5 × 38·6	—
2	4966·4	—	—	—
2	4953·9*c*	—	—	229·9 = 6 × 38·3
2	4947·0*f*	—	—	—
2	4931·4	—	—	—
4	4916·9*c*	—	—	266·9 = 7 × 38·2
4	4903·5*b*	—	269·4 = 7 × 38·5	—
4	4878·2*c*	—	—	305·6 = 8 × 38·2
4	4865·8*b*	—	307·1 = 8 × 38·4	—
4	4842·3*c*	—	—	341·5 = 9 × 37·9

the lines of the magnetic rotation spectrum which correspond. It should be noted that Wood was able to arrange a number of the lines of the latter spectrum into five series of constant wave-number difference, and it is these series that are referred to in the lower half of Table XLV.

TABLE XLV.

WHITE-LIGHT FLUORESCENCE.

λ	λ	λ	λ	λ	λ
5505·3	5436·8	5364·2	5289·7	5210·1	5126·5
5500·4	5431·3	5351·2	5283·2	5203·4	5119·6
5496·0	5427·2	5345·0	5277·1	5193·8	5095·4
5490·5	5422·2	5338·7	5270·6	5186·9	5088·4
5485·9	5417·2	5333·0	5264·1	5180·1	5081·0
5481·0	5397·4	5326·8	5254·6	5173·1	5072·1
5476·0	5392·1	5320·8	5249·1	5166·0	5050·2
5458·2	5386·4	5314·8	5245·6	5159·7	5049·0
5453·3	5381·0	5308·6	5238·3	5148·3	5041·0
5448·2	5375·4	5302·9	5232·5	5141·2	5034·1
5443·2	5369·4	5296·0	5216·6	5133·2	5026·1

WHITE-LIGHT FLUORESCENCE AND MAGNETIC ROTATION SERIES.

Series.	White-light fluorescence.	Magnetic rotation.	Series.	White-light fluorescence.	Magnetic rotation.
5 ?	5296·0	—	1	5159·7	5159·1
4 ?	5289·7	5288·6	5	5148·3	5148·0
3 ?	5283·2	5282·6	4	5141·1	5140·8
2 ?	5277·1	5276·6	3	5133·2	5133·3
1 ?	5270·6	5270·3	2	5126·5	5126·3
5 ?	5264·1	5263·8	1	5119·6	5119·1
4 ?	5249·1	—	3	5095·4	5094·8
3 ?	5245·6	5243·0	2	5088·4	5087·4
2 ?	5238·3	5238·0	1	5081·0	5079·9
1 ?	5232·5	5232·2	5	5072·1	5071·8
1	5193·8	5192·3	2	5050·2	5048·3
5	5186·9	5186·5	1	5041·0	5040·2
4	5180·1	5179·6	5	5034·1	5033·3
3	5173·1	5172·9	4	5026·1	5025·1
2	5166·0	5165·8			

The red region of the white light resonance spectrum has not been fully resolved, but this spectrum is excited by the two lithium lines, $\lambda = 6708$ and 6104, and its lines have been measured. The values, however, are only accurate to within 2 or 3 A. It is very interesting to note that that two series are present with $k = 54$ and 63 respectively, instead of 38, as in the greenish-blue region. From this Wood was able to detect two series in the positively-rotated magnetic lines for which $k = 63$ and 67 respectively. Orange-red resonance lines and the series in the positive magnetic rotation spectrum are given in Table XLVI.

TABLE XLVI.

LITHIUM EXCITATION ($\lambda = 7100 - \lambda = 5800$).

Wave-length.	Series A, $k = 54$. Series B, $k = 63$.
7074*b*	$366 = 6 \times 61$
7015*b*	$307 = 5 \times 62$
6965*b*	$257 = 4 \times 64$
6898*b*	$190 = 3 \times 63$
6834*b*	$126 = 2 \times 63$
6772*b*	$64 = 1 \times 64$
6708	
6643*b*	$65 = 1 \times 65$
6580*b*	$128 = 2 \times 64$
6519*b*	$189 = 3 \times 63$
6461*b*	$247 = 4 \times 62$
6396*b*	$312 = 5 \times 62$
6338*b*	$370 = 6 \times 62$
6277*b*	$431 = 7 \times 62$
6218*a*	$116 = 2 \times 58$
6158*a*	$56 = 1 \times 56$
6102	
6047*a*	$55 = 1 \times 55$
5998*a*	$104 = 2 \times 52$
5942*a*	$160 = 3 \times 53$
5896*a*	$206 = 4 \times 52$

SERIES IN THE POSITIVE MAGNETIC ROTATION ($\lambda = 7200$ TO $\lambda = 6000$).

Intensity.	Rotation.	Wave-length.	Series differences.
6	10	6761·9	$334{\cdot}7 = 5 \times 67{\cdot}7$
8	10	6692·9	$265{\cdot}7 = 4 \times 66{\cdot}4$
8	10	6624·2	$197{\cdot}0 = 3 \times 65{\cdot}7$
8	10	6557·4	$130{\cdot}2 = 2 \times 65{\cdot}1$
8	10	6557·1	$129{\cdot}9 = 2 \times 65{\cdot}0$
8	10	6490·9	$63{\cdot}7 = 1 \times 63{\cdot}7$
8	10	6490·1	$62{\cdot}9 = 1 \times 62{\cdot}9$
10	10	6427·2	
8	6	6580·3	$130{\cdot}5 = 2 \times 65{\cdot}2$
6	6	6515·8	$66{\cdot}0 = 1 \times 66{\cdot}0$
6	6	6515·0	$65{\cdot}2 = 1 \times 65{\cdot}2$
10	10	6449·8	
8	10	6325·5	$124{\cdot}3 = 2 \times 62{\cdot}1$
8	10	6324·5	$125{\cdot}6 = 2 \times 62{\cdot}8$
8	10	6323·8	$126{\cdot}6 = 2 \times 63{\cdot}3$
6	6	6259·6	$190{\cdot}2 = 3 \times 63{\cdot}4$
6	8	6199·1	$250{\cdot}7 = 4 \times 62{\cdot}7$
7	8	6139·2	$310{\cdot}6 = 5 \times 62{\cdot}1$

Fluorescence and Phosphorescence.

It will be convenient to discuss the whole of the phenomena of luminescence, other than that of optical resonance, under one head,

owing to the fact that, although there is reason to believe that there is one essential difference between fluorescence and phosphorescence, both are evidences of the absorption of radiant energy at one wave-length or associated group of wave-lengths and its emission at another and larger wave-length or associated group of wave-lengths. This grouping together of the two phenomena is further favoured by the fact that, whilst a few instances of true and undoubted fluorescence can be dealt with separately, many investigations have been made which clearly demonstrate the simultaneous occurrence of both phenomena, and any attempt to sub-divide our treatment would obscure the issue and damage the true perspective of the whole problem. Accepting the persistence of luminescence as the true criterion of phosphorescence, though, as will be shown later, this is not strictly correct, we can clear the ground to a certain extent at the start by saying that phosphorescence has only been observed with substances in the solid state, and it is possible also that in some cases a crystalline structure is an essential condition. This does not mean that fluorescence is not observed without phosphorescence with solid and crystalline compounds. Many instances of crystalline organic compounds are known which exhibit marked fluorescence, typical examples being the hydrocarbons, anthracene and fluorene. Then again, we have the uranyl salts, which exhibit remarkably intense fluorescence, to be described in detail below. This statement means that the luminescence exhibited by gases, liquids, and solutions is always a manifestation of true fluorescence. This fact allows us first of all to discuss these instances and then to deal with the more complex question of the luminescence of solid substances.

Fluorescence of Gases and Solutions.—In the study of fluorescence there are two phenomena to be investigated, namely, the wave-lengths of the luminescence radiation and the relation between these and those of the radiation which excites them. The same is true, of course, for phosphorescence, but in this case there is the additional phenomenon of the rate of decay of the luminescence after the excitation has ceased. The wave-lengths of the exciting radiation in the case of gases, liquids, and solutions can readily enough be determined by the methods of absorption spectra, but in the case of solids a different method may be necessary. The absorption spectrum of a crystal can easily be measured if a transparent crystal layer of sufficient size is available. This method obviously is inapplicable to a fine powder, and it is a very difficult matter to determine the absorption spectrum in such cases. The region of the spectrum that induces the phosphorescence or fluorescence can be determined by projecting a complete spectrum upon a layer of the powder and observing where the luminescence is most intense. As will be seen later, this method was adopted by Lenard and Klatt in their work on phosphorescence.

The measurement of the wave-lengths of the luminescence radiation reduces itself to the projection of a sufficiently intense beam of

the radiation on to the slit of a spectroscope or spectrograph. This is not always as easy as it may sound, since the intensity of the fluorescence is often very small. Particularly is this the case with gases and vapours, and sometimes it is true with liquids and solutions. With solids, on the other hand, this difficulty rarely arises, because the luminescence, as a general rule, is sufficiently intense. Some of the methods which have been employed will be indicated below.

When fluorescence radiation is spectroscopically examined, it will generally be found that it extends over a broad band of wave-lengths, the intensity being greatest at, or near, the centre, and decreasing on either side of the maximum. In these cases one speaks of the whole as an emission band. Notable exceptions to this general rule have been observed in which spectroscopic analysis reveals a definite structure in the emission band, that is to say, the band is resolved into an associated group of sub-groups, which are symmetrically distributed about a central sub-group of maximum intensity. Several organic compounds show a structure of this type in their fluorescence spectra. The most striking evidence of resolution is given by the uranyl salts, in which each sub-group is found to consist of about five subsidiary groups. It is of more than passing interest to note that, where observation has rendered comparison possible, the absorption bands, to which the luminescence is due, exhibit a structure of a similar type without, however, the intervals between the sub-groups in the two bands being necessarily identical. It would seem in the highest degree probable from this that where resolution is not observed the intensity curve of the emission band is the envelope of a series of associated wave-lengths which, for some reason as yet unexplained, cannot be disentangled. By the use of spectrophotometric methods Howes has succeeded in proving the presence of sub-groups in many emission bands previously considered as unresolved. The same general statement is true as regards absorption bands, many of which remain unresolved into their components, but it is only right to say that advances are steadily being made in this direction also. The close analogy between emission bands and absorption bands is evidenced by the fact that each, when resolved into sub-groups, exhibits constant wave-number intervals between them. We may now discuss the work which has been carried out on the fluorescence of gases and solutions.

The fluorescence of mercury vapour was first observed by Hartley,[1] who found that a bluish-green fluorescence was emitted when the vapour was excited by the rays from the spark between lead-cadmium or tin-cadmium electrodes. He further noted that the fluorescence was most brilliant when the mercury was in brisk ebullition, and that it ceased when all the metal had been converted into vapour above the boiling-point.

The phenomenon was next investigated by R. W. Wood,[2] who found that the fluorescent spectrum of the vapour in vacuo extended from

[1] *Proc. Roy. Soc.*, A, **76**, 428 (1905).

[2] *Phil. Mag.*, **18**, 240 (1909).

the yellow to about 3000 A. with a very pronounced minimum intensity at 3600 A. In a later paper van der Lingen and Wood [1] described a detailed investigation of the phenomenon, the objects of which were to determine the exact conditions under which the fluorescence takes place, and the correlation between the excitation in the various absorption bands and the fluorescence emission. They proved in the first case that it is impossible to excite the fluorescence in quiescent mercury vapour, but only in vapour which is being distilled from the metal at a temperature of 150° or higher. It is thus made clear that the fluorescence is a property of active molecules of vapour which differ in some way from the normal monatomic molecules present in the quiescent vapour. This is not true of the resonance radiation obtained when the vapour is excited by the line at $\lambda = 2536$ A. emitted by a quartz mercury lamp.

In his earlier work Wood found that this line is emitted by mercury vapour when excited by light of the wave-length 1890 to 1860 A., and it is of some importance to determine whether this emission depends on the age of the vapour. In order to decide this point bulbs containing mercury vapour were exposed by van der Lingen and Wood to the aluminium lines at about 1860 A., in one case with the vapour in the active state and in the other case in the quiescent state. In the latter an exposure of two minutes gave only a trace of the 2536 line on the photograph, whereas in the former an exposure of two seconds only gave this line with the same intensity. It follows that mercury vapour in the active state, when excited by the short wave ultra-violet radiation, emits the 2536 line with an intensity about sixty times greater than it does in the quiescent state.

As regards the correlation between absorption and fluorescence, the first matter which concerns us is the absorption spectrum of mercury vapour, and this, according to van der Lingen and Wood, is as follows :—

1. A strong absorption line at 2536 A. and a weaker one at 2539 A.
2. Four lines at 2346, 2339, and 2331 A., which fuse together with rise of temperature, forming a band which gradually extends towards the shorter wave-lengths with increasing vapour density.
3. A strong absorption line at 1849 A. corresponding to the strong emission line at this wave-length.
4. Two strong and very unsymmetrical absorption bands, one with its head close to the 2539 line and the other with its head near 1849 A. With increasing vapour density, these bands gradually extend towards the longer wave-lengths.

The complete fluorescence spectrum consists of :—

1. A symmetrical structureless band, extending from the red to $\lambda = 3700$, with its maximum at $\lambda = 4850$.
2. A similar broad band with maximum at $\lambda = 3300$, the two bands fusing together with long exposures.

[1] *Astrophys. Journ.*, **54**, 149 (1921).

3. An unsymmetrical faint band coinciding with the absorption band just above $\lambda = 2539$.

4. A somewhat unsymmetrical band extending from $\lambda = 2349$ to 2100 A.

5. The lines at $\lambda = 2536$ and 2539 A.

We may now consider the excitation of the fluorescence by definite wave-lengths and take first the radiations lying within the 1849 absorption band. This band begins at $\lambda = 1849$ A., and extends towards the longer wave-lengths with increasing vapour density, reaching $\lambda = 2200$ A. at about 280°, with a 10 cm. column of mercury vapour. When excitation is caused by the aluminium line at $\lambda = 1854$ the visible fluorescence commences at 210° and consists of the 2536 line and the broad band in the green-violet with maximum at $\lambda = 4850$. With increased vapour density, the 2536 line becomes weaker, the green-violet band is more intense, and the ultra-violet band, with maximum at 3300, appears and becomes stronger as the 2536 line decreases in intensity.

The same is observed when the group of aluminium lines at $\lambda = 1862$ to 1854 is used, but in this case the ultra-violet fluorescence band is visible at the low density, and at the higher density it is as strong as the green-violet band.

This suggests that the ultra-violet absorption band is in reality a complex of several bands, each being associated with an emission band. In this case the green-violet fluorescence band would be associated with the component of the absorption band which falls just above the 1849 line, the ultra-violet fluorescence band with a component of the absorption band of somewhat longer wave-length, and if there were a third component of still longer wave-length, this would be associated with a third fluorescence band of smaller wave-length. This is actually the case, since, on excitation by the group of zinc lines at $\lambda = 2150$ to 2000 A. a fluorescence band appears at $\lambda = 2349$ to 2100 A. This band is approximately in the same position as the fluted band described by Steubing,[1] which, however, van der Lingen and Wood failed to observe.

This new ultra-violet fluorescence band at $\lambda = 2346$ behaves in a manner quite different from the other two fluorescence bands. It is excited in its entirety by the group of four zinc lines at $\lambda = 2138$, 2099, 2061 and 2024 A. When excitation is caused by each of these lines in order, the region of maximum intensity in the fluorescence band moves towards the shorter wave-lengths, *i.e.* excitation by the 2024 line gives only the portion of the fluorescence band of longer wave-length, whilst excitation by the 2138 line gives only the short wave portion of the band.

If excitation is caused by still longer wave-lengths, utilising a group of cobalt lines in the region of the absorption lines at $\lambda = 2346$ A. the green-violet and the next ultra-violet (3300) fluorescence bands are

[1] *Phys. Zeitsch.*, **10**, 787 (1909).

obtained with uniform intensity. The same is true when excitation is caused by the mercury line at $\lambda = 2536$.

There remains the absorption band just above $\lambda = 2539$, and excitation by a line within this band also gives the green-violet and ultra-violet bands of uniform intensity.

If mercury vapour is excited by all the aluminium lines of shorter wave-length than $\lambda = 2360$, a faint fluorescent line appears at $\lambda = 2346$ when the vapour is slowly distilling. This line increases in intensity as the vapour density increases, but it is soon merged in the extreme ultra-violet fluorescence band, which increases relatively faster in intensity. In addition to this line at 2346 A., which was first observed by Steubing, and the fluorescence band in this region, the lines at 2536 A. and 2539 A. and the green-violet and ultra-violet (3300) fluorescence bands are also emitted.

As has already been said, the fluorescence of many organic compounds has long been known, and during recent years our knowledge of this phenomenon has been greatly extended. From time to time theories have been brought forward to explain it, some of them based on purely chemical arguments. These, however, have not survived, and, therefore, do not need mention. Until 1907 it was believed that fluorescence only took place in the visible region and that compounds did not fluoresce if no emission of light were visible to the eye. In 1907, however, Stark [1] showed that ultra-violet fluorescence is a frequently-occurring phenomenon, and that many organic compounds exhibit strong luminescence, consisting of invisible ultra-violet light, and caused by the absorption of light of still shorter wave-length. Since then a considerable number of compounds have been recorded as having the power of ultra-violet fluorescence, and the wave-lengths of the emission bands measured.

It is of some interest that in the domain of organic chemistry the phenomenon of fluorescence is almost entirely restricted to homocyclic and heterocyclic compounds, it being very doubtful whether any aliphatic compound exhibits this property. Amongst the former group we find many benzenoid compounds including benzene and its homologues, also many naphthalene and anthracene derivatives, together with pyridine, pyrrole, and compounds which are derived from them. Further, it would seem that the presence of strongly acidic groups, such as $-NO_2$, tend to depress the power of fluorescing, whilst strongly electropositive groups, such as $-OH$ and $-NH_2$, tend to enhance it. No satisfactory explanation seems to have as yet been found of these facts.

A further fact may be mentioned, and this would seem to be of some importance. In the case of all organic compounds which exhibit fluorescence, and, indeed, of all compounds which exhibit this phenomenon without any simultaneous appearance of phosphorescence, the interval between the luminescence emission band and the absorption band at which the excitation takes place is relatively small, that is to

[1] *Phys. Zeitsch.*, **8**, 81 (1907).

say, the two bands are closely situated in the spectrum. Very frequently a certain amount of overlapping is found, the extreme short wave side of the emission band being superimposed on the extreme long wave side of the absorption band. This phenomenon, which will be subsequently referred to in greater detail, has led some observers to state that Stokes' law is disobeyed. This seems, however, to be a misconception of the phenomenon, the more probable explanation being that it is due to the association of subsidiary frequencies with the principal frequency, this association being secondary to the main phenomenon of absorption of energy and its subsequent radiation.

The experimental technique of fluorescence spectra observation is simple in the case of organic substances, which are generally examined in solution in some diactinic solvent, such as water, alcohol, hexane, etc. The fluorescence of the uranyl salts requires special discussion, in view of the great value of the results that have been obtained. In the case of solutions of organic compounds, a matter of the first importance is the absence of all suspended matter. If such is present the particles scatter the incident light with the result that the spectrum of the fluorescence is contaminated by the spectrum lines of the source of the exciting light. For this reason the presence of dust particles in the solution can at once be recognised. A beam of light from the selected source is directed by means of a lens on to the solution which is contained in a vessel provided with a quartz window, so as to allow the maximum transmission of the ultra-violet rays. The resulting fluorescence is examined along an axis which is at an angle with that of the beam of the exciting light, so as to guard against any portion of the latter finding its way, either by reflection or in any other way, into the observing spectroscope or spectrograph. Various forms of vessels have been used to hold the fluorescent solution. For example, Dickson,[1] in his investigation of the fluorescence of many organic compounds used the apparatus shown in Fig. 68, which consists of a glass tube about 4 cm. long and 1·5 cm. wide. At one end a U-shaped opening is made in the wall, as shown, and then, after the end has been ground flat, a quartz plate is cemented on with water-glass and asbestos. The other end of the tube is drawn out and bent up, this opening being left for convenience in cleaning the apparatus before use. The tube is mounted horizontally with the quartz plate close to the slit of the spectrograph, and is always filled with solution up to the same height. The solution is illuminated from above by a strong beam of light directed by means of a quartz lens through the U-shaped opening. For certain purposes Dickson used a glass tube about 4·5 cm. long and 1·5 cm. wide, with its two ends ground flat, and at right angles to the axis. To one end of this tube was cemented

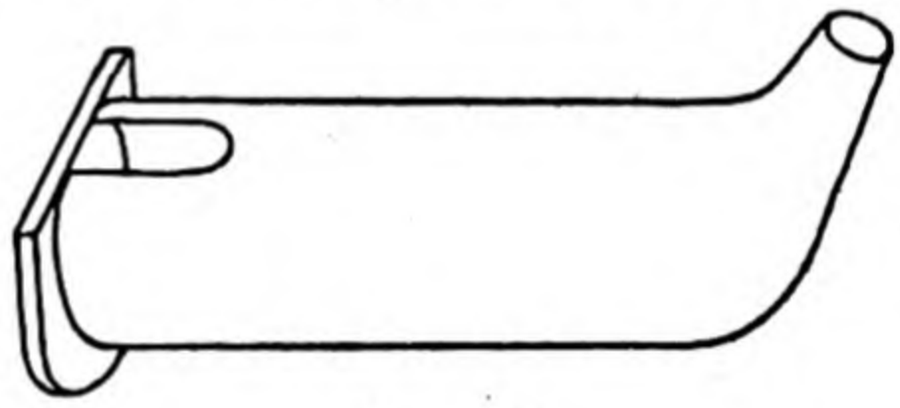


FIG. 68.

[1] *Zeitsch. wiss. Phot.*, **10**, 166, 181 (1912).

a flat quartz plate, and the tube was held in a vertical position with the quartz plate at the lower end. The vessel was partly filled with solution and the beam of exciting light was directed into the solution from below, through the quartz plate. On the upper end of the tube a short focus quartz lens rested, and this concentrated the fluorescence light, after reflection by a plane nickel mirror, on to the slit of the spectrograph. This method has the advantage of giving greater intensity of the beam of fluorescent light, but care is required so as to adjust the angle of incidence of the exciting light that no portion of it reaches the upper quartz lens.

An alternative method is to use a rectangular cell made of quartz which is placed directly in front of the spectrograph slit. On top of this cell is placed a right-angle prism of quartz, sufficient solution being placed in the cell to bring it into contact with the lower face of the prism. The beam of exciting light is directed by a lens on to the vertical face of the prism, and then, after total reflection by the prism, the light enters the solution. A convenient form of apparatus, when the volume of solution is of little importance, is shown in Fig. 69, and consists of a tube B, into which is fitted another tube A, by means of a ground glass joint. C and D are two quartz plates, which are cemented on with some suitable form of cement. The solution to be examined is placed in B, and the beam of exciting light is passed through A and brought to a focus at C. The fluorescence is produced in the immediate neighbourhood of C, and may be viewed through the tube D. The bulb and the side tube F serve for filling the tube with the solution.

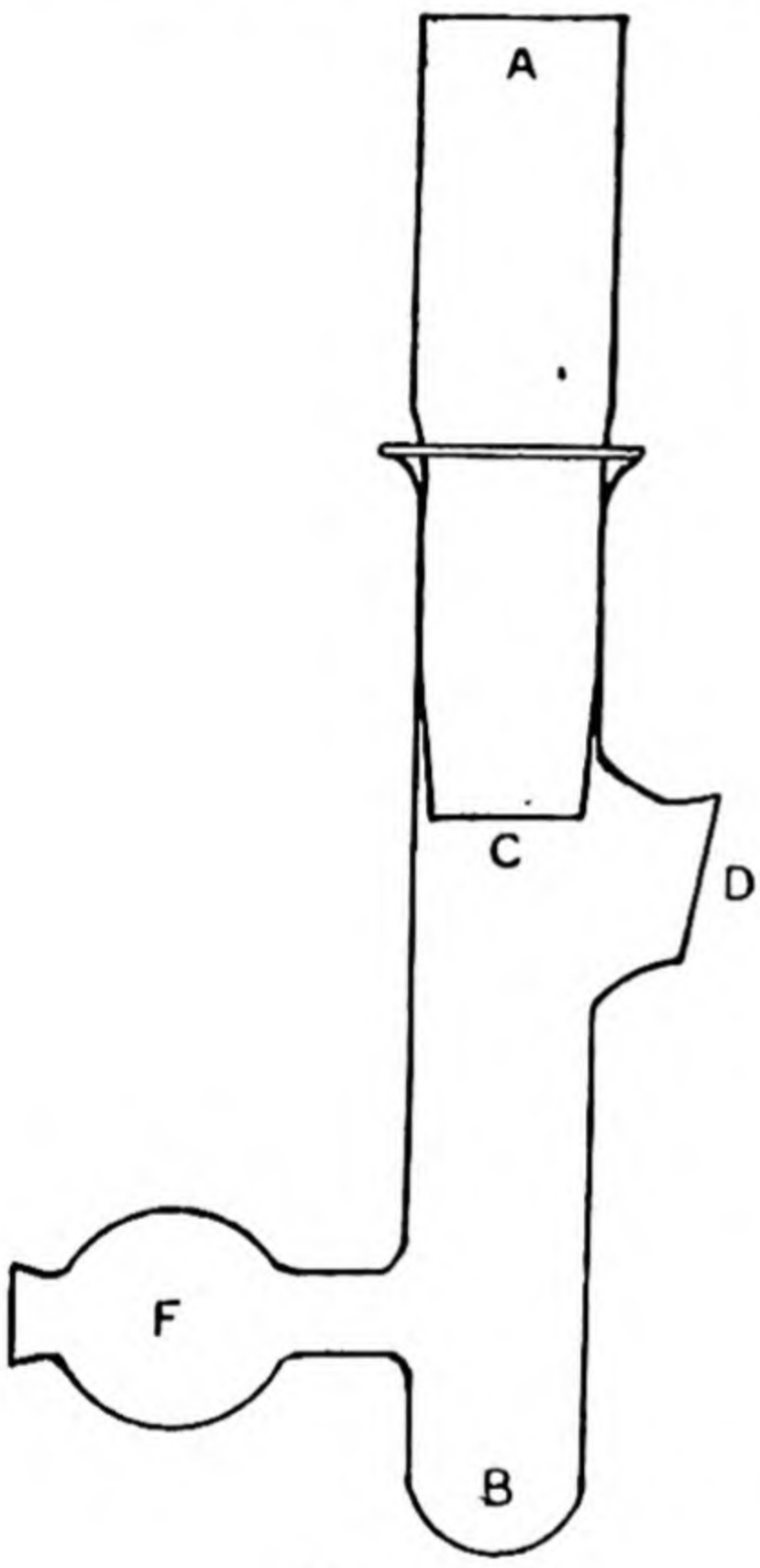


FIG. 69.

Two or three points arise in connection with the observation of fluorescence of solutions with the apparatus that has been described. In the first place, it will be found that the concentration of the solution is of some importance, since if it is too great the fluorescence is concentrated too much in the surface layer and, therefore, is difficult to observe. If, on the other hand, the solution is too dilute, the fluorescence becomes too widely spread for convenient observation. Then again, it is probable that the total intensity of the luminescence is dependent on the concentration.[1] Although this has not been

[1] Valentiner and Rossiger, *Preuss. Akad. Wiss.*, Berlin, **16,** 210 (1924).

actually demonstrated in the case of pure fluorescence, it is undoubtedly true with solid solutions which exhibit fluorescence and phosphorescence simultaneously. It would seem that, in general, the most suitable concentration to use is of the order of M/200, where M stands for one gram molecule in a litre of solution.

The second point concerns the choice of the source of the exciting light. It is obvious that the best results will be obtained by the use of light which is rich in rays having wave-lengths which lie within the absorption band of the substance under investigation. In general, these absorption bands lie in the ultra-violet and any source which gives a spectrum rich in ultra-violet lines will prove suitable. The arc between poles of high speed steel alloys, the spark between brass electrodes, either of these serves admirably.

A third point arises when the fluorescence lies in the ultra-violet, and is therefore invisible to the eye. The adjustment of the apparatus so as to obtain the optimum illumination of the spectrograph slit then becomes less easy. A convenient method of surmounting the difficulty is to mount the cell containing the solution in a suitable stand, so that when the cell has been brought into the correct position it may be removed and replaced in that position. The cell is filled with some solution which shows visible fluorescence and the whole apparatus brought into correct adjustment. The cell is then removed from its stand, and filled with the solution having invisible fluorescence, and replaced in its original position without any of the other component parts of the apparatus being disturbed.

It will be remembered that the exciting light is absorbed over an associated group of frequencies which is known as the absorption band, the emission band also consisting of an associated group of frequencies. It is customary to utilise the whole group of absorption frequencies in exciting fluorescence, but it is possible by the use of a monochromatic illuminator to excite the luminescence by means of a single spectrum line lying within that group. This can be done quite easily by using a small rectangular quartz cell, containing the solution, which is placed right up against the second slit of the monochromator.[1] The observing spectroscope or spectrograph may then be brought close to the quartz cell and so adjusted that the narrow strip of fluorescence can be seen. Some investigations have been carried out in this direction with very interesting results. Some years ago, in examining the fluorescence of organic compounds in solution, I found that the whole of the fluorescence band is emitted when excitation is brought about by any single spectrum line, the wave-length of which lies within the absorption band of the substance. This has also been proved in a rigid way by Nichols and his co-workers in their classic investigation of the uranyl salts.

Mention has already been made of the fact that in certain cases the broad fluorescence band usually observed can be resolved into

[1] For a description of this instrument, see Vol. I., p. 110.

sub-groups. Dickson [1] was the first to observe this phenomenon with organic compounds, and he showed further that the sub-groups of a single band can often be arranged in a series with constant frequency differences. The existence of these series of sub-groups with constant frequency differences has been conclusively established in the uranyl salts, and here also the additional information is forthcoming that the absorption band is also resolved into sub-groups with constant frequency difference. We thus learn that the structures of fluorescence and absorption bands are very similar in type, a fact that must have considerable weight in formulating any theory of the phenomenon of luminescence.

Since it is known that absorption bands are more readily resolved into their components when substances are examined in a state of vapour, the same may be expected to occur in fluorescence bands. Little work has been done on the fluorescence of organic compounds in the state of vapour, but reference must be made to one striking instance, namely, the fluorescence emission of benzene vapour which was observed and analysed by McVicker and Marsh.[2] The experimental method was simple in the extreme. A silica tube about 10 cm. long and 2 cm. wide, closed at one end with a quartz window and at the other with a rubber stopper fitted with an inlet and an outlet tube, was set up in front of the slit of a spectrograph, the distance between quartz window and slit being about 2 cm. To one side of the quartz window and at a distance of about 4 cm. was placed a spark gap with iron electrodes, and the gap was surrounded by a screen with a slot cut in it, so as to allow a beam of the light from the spark to fall on the benzene vapour immediately behind the quartz window. The inlet tube was connected to a flask of pure benzene, and the outlet tube to a filter pump through a flask cooled by means of ice. On starting the filter pump a stream of benzene vapour passed through the silica tube from the flask containing the benzene to the cooled flask. After a time, owing to the rapid evaporation, the benzene solidified and the pressure fell to 3 cm. The intensity of the fluorescence was small, but after an exposure of 100 minutes a photograph was obtained which, though somewhat lacking in density, enabled 38 sub-groups to be measured. A similar result was obtained when the iron arc was substituted for the iron spark.

It may be noted that Dickson recorded his inability to detect any evidence of the fluorescence of benzene vapour, and it is possible that the success achieved by McVicker and Marsh is due to their maintaining a stream of freshly-formed benzene vapour through the isolated silica tube, and that in this we have a phenomenon similar to that recorded by Hartley and by Wood in their investigations of the fluorescence of mercury vapour.

The actual values of the wave-lengths and wave-numbers of the

[1] *Zeitsch. wiss. Phot.*, **10**, 166, 181 (1912).
[2] *Trans. Chem. Soc.*, **123**, 820 (1923). See also p. 286.

fluorescent bands of benzene need not be given here, since they will be recorded later in connection with the Tesla luminescence spectrum of benzene. It may be noted, however, that their wave-numbers may be arranged in a system of series of constant difference. As will be shown, this resolution is exactly similar to that observed in the case of the uranyl salts.

Reference may be made here to the theory brought forward by Perrin,[1] which attributes the phenomenon of fluorescence to a definite chemical change. He shows that intense illumination of fluorescent solutions causes a gradual disappearance of the fluorescing compound. The velocity of this disappearance is a maximum when the solution is dilute and the fluorescence intensity is a maximum.

The action of light on fluorescent compounds has been investigated by R. W. Wood,[2] with particular reference to Perrin's theory that the phenomenon of fluorescence is connected with chemical change. By operating with a very intense beam of light, obtained by concentrating sunlight with a 6-inch lens of short focus, he succeeded, not only in proving that certain fluorescent compounds are changed chemically by the light, but also in preparing sufficient of the products to study their chemical and physical properties. The time required to effect the change varies with the substance, eosine is completely changed in two or three minutes, whilst rhodamine requires several hours. Usually a fluorescent substance under the action of light gives a coloured non-fluorescent substance which is converted by further action of the light into a colourless compound.

Fluorescein gives first an orange-red compound which is non-fluorescent, and this body is finally converted into a colourless substance. The results with eosine are the same, with the difference that the action of the light is more rapid. Rhodamine in aqueous solution is slowly bleached by light without the formation of an intermediate coloured form. In alcholic solution the dye is converted into an intermediate form which exhibits a strong green fluorescence, which is very different from the orange-red fluorescence shown by rhodamine itself. The intermediate body is soluble in water and the solution exhibits the same green fluorescence, which is interesting in view of the fact that this body is not formed by the action of light on an aqueous solution of the dye. Several other compounds were investigated and gave analogous results. The intermediate compounds exhibit absorption spectra which are different from those of the parent compounds, this not being surprising since the colour of the two are different.

In view of the very great intensity of the light used in these experiments, it is more than probable that Wood was dealing with photochemical reactions which had nothing whatever to do with fluorescence. The photochemical change of substances which are not fluorescence is a phenomenon made familiar by the work of Berthelot

[1] *Ann. der Phys.*, **10**, 133 (1918); *Comptes Rendus*, **177**, 612, 665 (1923).
[2] *Phil. Mag.*, **43**, 757 (1922).

and Gaudechon, and consequently there is no reason to assume any connection with the fluorescence of the dyestuffs used by Wood. That this is so is indicated by the fact that the intermediate compound given by fluorescein is non-fluorescent, and that this is photochemically converted into a colourless compound.

Still more convincing proof of this view is given by McLennan and Cale,[1] who show that the destruction of æsculin by light is a photochemical phenomenon, and has nothing to do with fluorescence. This was clearly demonstrated by the fact that aqueous solutions of æsculin which had been deprived of all dissolved air lost no fluorescent power after exposure in glass tubes for thirty hours to the rays from the quartz mercury lamp, although the solutions were strongly fluorescent during the whole period. When a similar solution which had again been ærated was exposed in glass vessels to the same light, the fluorescence decreased to one-third of its original value in 3·5 hours.

McLennan and Cale also made the important observation that when a solution of æsculin deprived of air was exposed in sealed quartz vessels to the light, the fluorescence fell to one-fifth of its value in two hours. This proves quite definitely that it is the ultra-violet rays of short wave-length which cause the photochemical transformation, and that this is not due to the rays which stimulate the fluorescence. This observation was confirmed by Miss Kearney.[2]

Fluorescence of the Uranyl Salts.—We may now turn to the fluorescence of the uranyl salts, which has formed the subject of a most exhaustive study. Indeed it may be said that this constitutes the most valuable contribution to our knowledge of the phenomenon. The experimental technique employed requires no special mention, except in so far as concerns individual branches of the whole investigation, for which the apparatus and methods used will be described when such is necessary. With rare exceptions, the whole of the investigation has been carried out with pure crystalline salts and not solutions. The excitation was carried out by light, as in all the experimental work with which we have, up to the present, been concerned.

The fluorescence exhibited by the uranyl salts has long been known, and has formed the basis of many investigations. The earliest work of importance was that of Stokes,[3] who was led from a study of the absorption and fluorescence of the well-known uranium glass to investigate the phenomena, as exhibited by uranyl nitrate, phosphate, acetate, and oxalate, and by certain uranium minerals, such as autunite (uranyl calcium phosphate) and chalcocite (uranyl copper phosphate). Stokes was the first to arrive at the conclusion that there is an intimate connection between the absorption of light by these substances and their fluorescence, and he also noted that the fluorescence and absorption spectra consisted each of a series of bands,

[1] *Proc. Roy. Soc.*, **102**, 256 (1922).
[2] *Phil. Mag.*, **47**, 648 (1924).
[3] *Phil. Trans.*, **142**, ii. 463 (1852); **143**, i. 385 (1853).

the intervals between which, as seen with a prism spectroscope, increase towards the shorter wave-lengths.

During his work on phosphorescence, E. Becquerel studied the uranyl salts and extended considerably the observations made by Stokes. In one of his papers Becquerel[1] gives the following conclusions amongst others :—

1. The uranous salts are not fluorescent or phosphorescent, this property being confined to the uranyl salts, most of which exhibit this phenomenon.

2. The luminescence spectrum consists of bands, from five to seven in number, which lie between the H_α and H_β lines.

3. When viewed with a prism spectroscope, the intervals between consecutive bands increase towards the shorter wave-lengths. Expressed in wave-numbers, the intervals are nearly constant.

4. The positions of the bands differ with different salts, and the same is true of the bands of the absorption spectra. The absorption bands seem to form a continuation of the series of the luminescence bands.

The study of this phenomenon was carried further by Morton and Bolton,[2] who investigated a very large number of uranyl compounds. These authors noted the following additional facts :—

1. The distribution of intensity in the luminescent spectra is such that the central bands are the brightest, the bands on the red and violet sides being progressively weaker.

2. The fluorescence spectrum overlaps the absorption spectrum in each case.

3. The positions of the fluorescent bands shift when the salts are dissolved in water or other solvents.

4 There is a marked difference between the spectra given by the same salt in the anhydrous and hydrated states.

A very interesting observation was made by H. Becquerel and Onnes,[3] who showed that at the temperature of liquid air each band of the spectrum is resolved into a group of much narrower bands, the homologous components of these resolved groups forming series with constant wave-number difference. Although they succeeded in extending their observations to the temperature of liquid hydrogen, no further resolution took place, the fine bands merely becoming narrower until they almost appeared as bright lines.

For an exhaustive study of the fluorescence of the uranyl salts we are indebted to Nichols who, in conjunction with Merritt, Howes, and Wilber, together with Miss Wick and Miss McDowell, carried out a long series of very valuable investigations of this phenomenon. A full account of this work was published in 1919 by Nichols and Howes,[4]

[1] *Comptes Rendus*, **75**, 296 (1872).
[2] *Chem. News*, **28**, 47, 113, 164, 173, 244, 257, 268 (1873).
[3] *Communications from the University of Leiden*, 110 (1909).
[4] "The Fluorescence of the Uranyl Salts," *Carnegie Institute Publications*, No. 298. Washington, 1919.

and the following account of their work is taken from that memoir.

In view of the fact that the fluorescence spectrum of the uranyl salts consists of seven or eight bands or band groups, one of the first points of interest which arise is whether the whole of these belong to one co-ordinated whole or whether the individual band groups are due to excitation by a specific wave-length. In order to put this question to the test, various salts were excited by various wave-lengths lying within the region of absorption and the relative intensities of the various bands measured with a spectro-photometer. Many such experiments were made under widely differing conditions without altering the relative intensities of the groups. The envelope curve of the fluorescence spectrum is single-crested, and is not modified in position or form by changing the mode of excitation. The spectrum, therefore, appears to be a single unit, which consists of resolved components, and, therefore, differs from many other bands of this type. This conclusion, reached in the early stages of the work, was strengthened and confirmed by later work. It would seem to be one of the most important results obtained.

Reference has already been made to the observations of E. Becquerel on the phosphorescence of the uranyl salts, by which is meant the persistence of the luminescence after the exciting radiation has been cut off. This phenomenon was fully investigated by Nichols and his colleagues from two points of view. The first question which arises is the rate of decay of the luminescence after the excitation has ceased. The second question is whether the phosphorescent emission is the same as the fluorescent emission, since, in the absence of any theoretical explanation of the phenomenon, it is possible to consider that the process which prepares a substance for phosphorescence might produce emission during excitation differing from that which constitutes phosphorescence, and which, together with the latter, would be present during fluorescence. Further, it is just possible that there may be present in the phosphorescence some components which require a measurable time for development, and, therefore, will be observable only after a definite interval of time. Owing to the characteristic structure of their fluorescence spectrum the uranyl salts offer an excellent opportunity of testing these possibilities.

The method of experiment consisted in the use of a rotating sector. The salt used was enclosed in a flat glass tube about 8 cm. long and 2 cm. wide, and this tube was mounted at right angles to the radius of the rotating sector. The salt was excited 120 times a second, while hidden from view by the closed sectors and was visible for 1/240 second during the passage of the open sectors. Under these experimental conditions a phosphorescent substance with a slow rate of decay will appear of equal brightness along the whole length of the glass tube, whilst a substance with a fast rate of decay will appear very bright at the bottom of the tube and barely visible at the top. In the case of the uranyl salts, the rate of decay is so rapid that the

intensity of luminescence at the top of the tube at 0·003 second after excitation is only a small fraction of that at the lower end at 0·0005 second after excitation.

As regards the spectra of phosphorescence, all the seven bands of the fluorescence spectrum were visible, unaltered in position and in relative intensity. The two spectra were found to be absolutely identical, each component band decaying at the same rate.

In addition to the above, observations were made of the rate of decay of the luminescence and also of the effect of infra-red light. It is well known that, in general, when phosphorescing materials are exposed to infra-red radiation the luminescence is temporarily enhanced and then ceases altogether. It was found, however, that in the case of the uranyl salts exposure to red and infra-red radiation had no accelerating effect on the rate of decay.

There is no need to describe in detail the measurements of the rate of decay of the phosphorescence caused by stimulation by light, and the following summary of the results obtained may be given :—

1. All uranyl salts exhibit the same type of phosphorescence, which has an increasing rate of decay instead of a decreasing rate, as is usual in true phosphorescence.

2. This is true, not only of the crystalline salts, but also of uranyl compounds in solid solution (uranium glass) or in the plastic state characteristic of the double phosphates.

3. The initial brightness and, to some extent, the rate of decay of the phosphorescence under similar excitation varies greatly with the different salts.

4. The intensity of the luminescence of a salt newly prepared in darkness is greater when first excited than subsequently, but soon reaches a stable condition.

5. Exposure to red and infra-red rays has no effect on the rate of decay.

6. The phosphorescence, like the fluorescence, of the uranyl salts appears to be independent of the mode of excitation, and the structure of the spectrum is the same during excitation and throughout the observable phosphorescent interval.

7. The rates of decay are not continuous, but occur in definite steps, there being at least three successive processes within the observed interval of about 0·006 second. These processes follow the law that $I^{-\frac{1}{2}}$, and the time are in linear relation.

8. The first and second processes, counting from the close of excitation, are of nearly equal duration, increasing in duration with the intensity of excitation in such a manner that the duration of the process is approximately proportional to the natural logarithm of the excitation.

9. In certain salts, such as uranyl ammonium nitrate, the rate of decay is retarded by cooling, but in other cases the effect is slight.

10. Uranyl nitrates, with 2, 3, and 6 molecules of water of crystallisation, differ greatly in the rate of decay, but the changes in

crystalline form appear to be more important in this respect than the amount of water.

11. In the case of the polarised spectra of the uranyl double chlorides, to be referred to later, both components decay at the same rate, and no change in relative brightness can be detected throughout the range covered by the observations.

In my opinion the phenomenon of the " phosphorescence " of the uranyl salts under excitation by light is not one of true phosphorescence at all, in spite of the fact that it has a measurable persistence. When we come to discuss the theoretical aspect of the phenomena of fluorescence and phosphorescence, it will be noted that these two may very probably be two entirely different manifestations of the same energy process, and that they can be differentiated by the relations between the wave-lengths of the exciting radiation and the luminescence radiation. The measurable period of persistence of the luminescence must not be accepted as a criterion of true phosphorescence, since we know that a molecule, which has been chemically activated by means of light, has a definite life period. Although these life periods as so far determined are much shorter than the decay periods described above, it must be remembered that little or nothing is known of the life period of activated molecules in the solid state.[1]

I hold the view that it is incorrect to apply the word phosphorescence to the phenomena observed when the uranyl salts are activated by means of light and, as will presently be shown, the wave-lengths of the activating radiation and the fluorescent radiation are closely situated in the spectrum. This view is supported by further work carried out by Miss Wick and Miss McDowell, and described by Nichols and Howes. When certain uranyl salts are activated by cathode rays at — 185° they luminesce for some minutes after the excitation has ceased. The salts investigated were uranyl potassium nitrate, $UO_2(NO_3)_2$, $2KNO_3$, and the corresponding sulphate, $UO_2SO_4K_2SO_4$. It was found, in the first place, that the luminescence spectrum was exactly the same whether excited by light or by cathode rays. Further, the double sulphate was first excited by light when the luminescence had no persistence to be observed by the eye, and then exposed to cathode rays which produced the same luminescence with, however, a persistence of several minutes. The effect of the cathode rays was cumulative, several records being necessary for complete excitation. When this luminescence had died away photo-excitation was resumed, and the whole sequence repeated many times without any observable change in the effect of the light.

The decay in the luminescence caused by cathode rays was examined, and its rate determined. It was then found that the decay curve was similar to those always observed with true phosphorescence, namely, two processes, the rate in the second being slower than that in the first. Under different conditions, the phosphorescence lasted

[1] This will be further discussed below on p. 341.

from less than a minute to ten or fifteen minutes. The exact form of the decay curve varied with the time of excitation, and the time of decay, increased with the time of excitation, though the initial intensity changed relatively little.

It would therefore seem that true phosphorescence occurs when the uranyl salts are excited by cathode rays and, in view of what was said above against the reality of the phosphorescence as such caused by photo-excitation, it is interesting to note that in the case of cathode rays the excitation takes place under conditions corresponding to a much smaller wave-length than in photo-excitation.

We may now deal with the structure of the fluorescence bands and also of the absorption bands at which the photo-excitation takes place. It was suggested by E. Becquerel that the two sets of bands form a consecutive series with equal wave-number intervals, and this view was also supported by H. Becquerel,[1] who studied the fluorescence and absorption of uranyl nitrate. It was also noted by the latter that two of the bands are reversible, appearing as emission bands when suitably excited, whereas if light free from exciting rays were passed through the substance, they appear as absorption bands. In the present work, this last observation has been confirmed and extended by the discovery that there are three reversible bands instead of two.

As regards the wave-number intervals between the bands, it was found early in the course of the work of Nichols and his colleagues

TABLE XLVII.

Absorption.			Fluorescence.		
μ.	$1/\mu \times 10^3$.	Interval.	μ.	$1/\mu \times 10^3$.	Interval.
0·4350	2298·9	—	—	—	—
—	—	62·8	—	—	—
0·4472	2236·1	—	—	—	—
—	—	68·8	—	—	—
0·4614	2167·3	—	—	—	—
—	—	66·5	—	—	—
0·4760	2100·8	—	0·4765	2098·6	—
—	—	68·3	—	—	**66·1**
0·4920	2032·5	—	0·4920	2032·5	—
—	—	**82·0**	—	—	83·2
0·5127	1950·5	—	0·5130	1949·3	—
—	—	—	—	—	83·6
—	—	—	0·5360	1865·7	—
—	—	—	—	—	81·9
—	—	—	0·5606	1783·8	—
—	—	—	—	—	83·4
—	—	—	0·5881	1700·4	—
—	—	—	—	—	84·9
—	—	—	0·6190	1615·5	—

[1] *Comptes Rendus*, **101**, 1252 (1885).

that these are approximately constant in both the fluorescence and absorption series, but that the absorption interval is notably less than the fluorescence interval. This observation was made with uranyl nitrate and uranyl potassium sulphate, the band groups of which are not resolved at 20°. The measurements for the latter salt are given in Table XLVII.

These measurements leave no doubt as to the difference in spacing of the bands in the absorption and fluorescence regions. The question of the reality of the coincidences between the three absorption and fluorescence bands in the "reversing" region cannot be answered from a study of spectra which are only resolved to the extent shown, namely, to the separate band groups. The same is true as regards the reality of the constant wave-number difference between the consecutive bands belonging to each series.

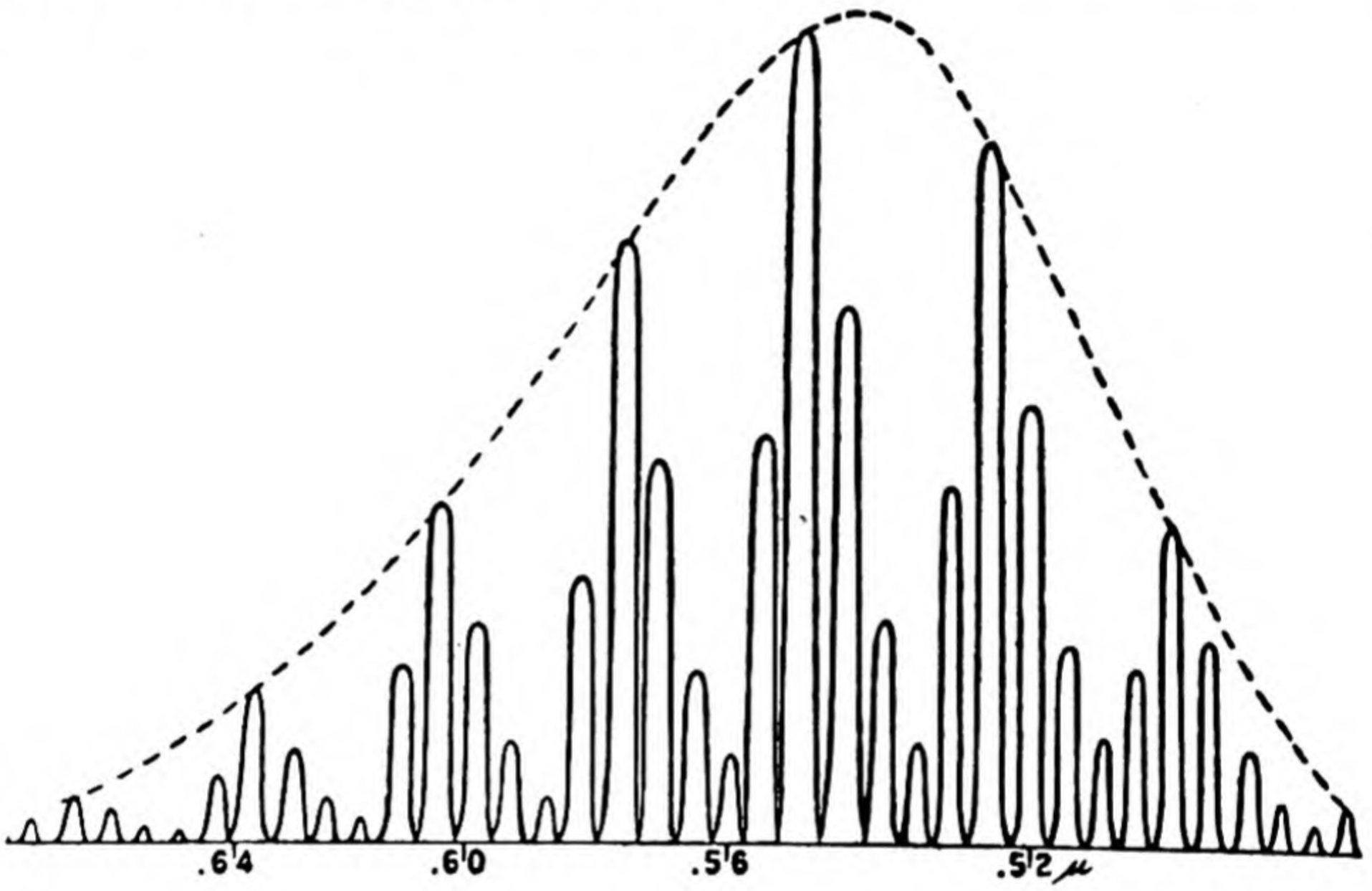


FIG. 70.

Our knowledge of the structure of the absorption and fluorescence spectra was very greatly advanced by the discovery that the bands specified in Table XLVII. are resolved into groups of small bands in the case of the uranyl chlorides, and still more by the discovery by Becquerel and Onnes that further resolution takes place at — 185°. The following double chlorides were employed :—

UO_2Cl_2, 2KCl, $2H_2O$	UO_2Cl_2, 2 RbCl, $2H_2O$
UO_2Cl_2, $2NH_4Cl$, $2H_2O$	UO_2Cl_2, 2CsCl.

These salts crystallise in triclinic plates which are strongly fluorescent, and their spectra, which are almost identical in structure, are resolved at room temperature into eight groups of narrow bands. Each group, which corresponds to a single band of the ordinary uranyl fluorescence spectrum (see Table XLVII.), consists of five nearly equidistant bands.

Each narrow band is well separated from its two neighbours, and is about one-tenth as wide as the unresolved band groups of the ordinary uranyl fluorescence spectrum. The curve which forms the envelope of the whole set of these band groups is similar to that of a fluorescence spectrum consisting of a single broad band, and the envelope of each resolved band group is similar to that of a single band group in a uranyl fluorescence spectrum that is not fully resolved.

The general appearance of the resolved band groups is shown in Fig. 70,[1] which is based on measurements made with ammonium uranyl chloride. The abscissæ are on a scale of wave-numbers, and the ordinates on a scale of intensities. The intensities of the bands at the extreme left and right are somewhat exaggerated, since, if drawn to scale, they would be scarcely visible. In what follows the five bands in each group, reading from red to violet, are designated by the letters B, C, D, E, and A, and all the bands in one spectrum having the same letter form homologous series of constant wave-number difference.

In order first to determine the intervals between the band groups, the position of what may be called the centre of each group was found by averaging the frequencies of all five bands. The intervals between these centres are given in Table XLVIII. for groups 2 to 7, groups 1 and 8 being omitted, except in the case of the ammonium salt, since sufficient data are unavailable.

TABLE XLVIII.

Group.	Potassium uranyl chloride.		Ammonium uranyl chloride.		Rubidium uranyl chloride.		Cæsium uranyl chloride.	
	Centre.	Interval.	Centre.	Interval.	Centre.	Interval.	Centre.	Interval.
1	—	—	1505·3	—	—	—	—	—
2	1587·2	—	1588·6	83·3	1591·5	—	1592·6	—
3	1670·8	83·6	1671·9	83·3	1674·9	83·4	1675·9	83·3
4	1754·0	83·2	1755·0	83·1	1758·3	83·4	1759·3	83·4
5	1836·6	82·6	1838·4	83·4	1840·7	82·4	1841·8	82·5
6	1919·6	83·0	1922·3	83·9	1924·2	83·5	1924·7	82·9
7	2003·3	83·7	2005·6	83·3	2007·8	83·6	2006·6	81·9
Average .		83·22	—	83·38	—	83·26	—	82·80

The tendency of the group intervals of the cæsium salt to diminish towards the violet is not an indication that the groups are made up of series with a diminishing interval, as will be explained below. In the case of the other salts the intervals are essentially constant.

As regards the bands within each group, they are not distributed with absolute symmetry, as may be seen from the average intervals between the bands which are set forth in Table XLIX.

[1] For permission to reproduce this and the following illustrations from Nichols and Howes' memoir I am indebted to the Carnegie Institution of Washington.

TABLE XLIX.

Uranyl salt.	Intervals between bands.				
	B to C.	C to D.	D to E.	E to A.	A to B.
UO_2Cl_2, 2KCl . .	15·97	18·66	17·96	14·70	15·58
UO_2Cl_2, 2NH_4Cl . .	17·56	17·74	17·86	15·67	15·67
UO_2Cl_2, 2RbCl . .	16·20	18·43	18·50	12·75	17·12
UO_2Cl_2, 2CsCl . .	18·25	12·85	18·63	14·52	18·10
Average . .	16·99	16·92	18·24	14·41	16·62

It is important to note the fact that the optical centre of each band group is almost coincident with the centre of the D band.

It has already been said that the individual bands denoted by the same letters form homologous series with constant wave-number intervals. The complete set of measurements are given below in Tables LI. and LII., and the average values for the five series are given in Table L.

TABLE L.

Series.	K.	NH_4.	Rb.	Cs.	Average by series.
B . . .	83·42	83·34	83·49	82·32	83·14
C . . .	83·11	82·99	82·97	82·50	82·89
D . . .	83·30	83·21	83·17	82·85	83·13
E . . .	83·00	83·81	82·97	83·45	83·31
A . . .	83·23	83·65	83·77	82·85	83·37
Average .	83·21	83·40	83·27	82·80	83·17

The discrepancies are not to be considered as entirely accidental, but as being due to the complex nature of each band, a fact which has been proved by their resolution at low temperatures.

TABLE LI.

Group and series.	Potassium uranyl chloride.		Ammonium uranyl chloride.		Rubidium uranyl chloride.		Cæsium uranyl chloride.	
	λ.	$1/\lambda \times 10^3$.	λ.	$1/\lambda \times 10^3$.	λ.	$1/\lambda \times 10^3$.	λ.	$1/\lambda \times 10^3$.
1 B	—	—	0·6809	1469·7	—	—	—	—
1 C	—	—	0·6716	1489·9	—	—	—	—
1 D	—	—	0·6635	1507·1	—	—	—	—
1 E	—	—	0·6571	1521·8	—	—	—	—
1 A	—	—	0·6501	1538·2	—	—	—	—
2 B	0·6436	1553·7	0·6430	1555·3	0·6420	1557·6	0·6401	1562·3
2 C	0·6375	1568·6	0·6358	1572·6	0·6354	1573·8	0·6336	1578·3
2 D	0·6303	1586·6	0·6291	1589·6	0·6281	1592·2	0·6289	1590·1
2 E	0·6225	1606·4	0·6231	1604·9	0·6206	1611·3	0·6219	1608·0
2 A	0·6171	1620·5	0·6172	1620·2	0·6162	1622·8	0·6156	1624·4
3 B	0·6111	1636·5	0·6103	1638·6	0·6098	1640·0	0·6090	1642·0
3 C	0·6051	1652·5	0·6041	1655·3	0·6030	1658·3	0·6015	1662·5
3 D	0·5983	1671·5	0·5978	1672·7	0·5967	1675·9	0·5970	1675·0
3 E	0·5919	1689·5	0·5923	1688·2	0·5903	1694·1	0·5911	1691·9
3 A	0·5869	1704·0	0·5866	1704·8	0·5860	1706·4	0·5854	1708·2
4 B	0·5816	1719·4	0·5813	1720·3	0·5800	1724·0	0·5789	1727·4
4 C	0·5759	1736·4	0·5752	1738·6	0·5742	1741·6	0·5729	1745·4
4 D	0·5698	1754·9	0·5696	1755·7	0·5686	1758·7	0·5689	1757·9
4 E	0·5642	1772·3	0·5642	1772·3	0·5625	1777·8	0·5631	1775·9
4 A	0·5595	1787·2	0·5593	1787·9	0·5588	1789·4	0·5587	1789·7
5 B	0·5551	1801·4	0·5546	1803·1	0·5537	1806·1	0·5529	1808·6
5 C	0·5497	1819·3	0·5492	1820·7	0·5486	1822·8	0·5472	1827·5
5 D	0·5442	1837·6	0·5436	1839·7	0·5430	1841·5	0·5433	1840·5
5 E	0·5390	1855·3	0·5385	1856·9	0·5377	1859·8	0·5379	1859·1
5 A	0·5349	1869·6	0·5342	1871·8	0·5339	1873·1	0·5339	1873·1
6 B	0·5306	1884·7	0·5300	1886·8	0·5291	1890·0	0·5288	1891·1
6 C	0·5259	1901·5	0·5250	1904·6	0·5248	1905·5	0·5234	1910·4
6 D	0·5208	1920·1	0·5200	1923·2	0·5195	1925·0	0·5198	1923·6
6 E	0·5159	1938·3	0·5153	1940·5	0·5145	1943·5	0·5147	1942·7
6 A	0·5119	1953·5	0·5112	1956·3	0·5110	1957·3	0·5113	1955·7
7 B	0·5078	1969·4	0·5072	1971·5	0·5066	1973·8	0·5067	1973·5
7 C	0·5039	1984·4	0·5031	1987·6	0·5027	1989·1	0·5024	1990·3
7 D	0·4990	2004·0	0·4986	2005·7	0·4979	2008·4	0·4989	2044·4
7 E	0·4946	2021·7	0·4940	2024·1	0·4935	2026·2	0·4937	2025·6
7 A	0·4909	2036·9	0·4904	2039·2	0·4899	2041·4	0·4904	2039·2
8 B	0·4869	2053·8	0·4867	2054·6	0·4857	2059·0	0·4863	2056·3
8 C	0·4836	2068·9	0·4829	2071·0	0·4824	2072·8	0·4819	2075·0

TABLE LII.

SERIES A.

		Group 1.	Group 2.	Group 3.	Group 4.	Group 5.	Group 6.	Group 7.
K	Frequencies (obs.)	—	1620·5	1704·0	1787·2	1869·6	1953·5	2036·9
	,, (calc.)	—	1620·5	1703·8	1787·0	1870·2	1953·5	2036·7
	Differences .	—	0·0	− 0·2	− 0·2	+ 0·6	0·0	− 0·2
	Intervals (obs.) .	—	83·5	83·2	82·4	83·9	83·4	
NH_4	Frequencies (obs.)	1538·2	1620·2	1704·8	1787·9	1871·8	1956·3	2039·2
	,, (calc.)	1537·2	1620·9	1704·5	1788·2	1871·8	1955·5	2039·1
	Differences .	− 1·0	+ 0·7	− 0·3	+ 0·3	0·0	− 0·8	− 0·1
	Intervals (obs.) .	82·0	84·6	83·1	83·9	84·5	82·9	
Rb	Frequencies (obs.)	—	—	1706·4	1789·4	1873·1	1957·1	2041·4
	,, (calc.)	—	—	1706·0	1789·7	1873·5	1957·3	2041·0
	Differences .	—	—	− 0·4	+ 0·3	+ 0·4	+ 0·2	− 0·4
	Intervals (obs.) .	—	—	83·0	83·7	84·0	84·3	
Cs	Frequencies (obs.)	—	1624·4	1708·2	1789·7	1873·1	1955·7	2039·2
	,, (calc.)	—	1624·6	1707·4	1790·3	1873·1	1956·0	2038·8
	Differences .	—	+ 0·2	+ 0·8	+ 0·6	0·0	+ 0·3	− 0·4
	Intervals (obs.) .	—	83·8	81·5	83·4	82·6	83·5	

SERIES B.

		Group 1.	Group 2.	Group 3.	Group 4.	Group 5.	Group 6.	Group 7.	Group 8.
K	Frequencies (obs.)	—	—	1636·5	1719·4	1801·4	1884·7	1969·4	2053·8
	,, (calc.)	—	—	1635·5	1718·9	1802·3	1885·7	1969·1	2052·6
	Differences .	—	—	− 1·0	− 0·5	+ 0·9	+ 1·0	− 0·3	− 1·2
	Intervals (obs.) .	—	—	82·9	82·0	83·0	84·7	84·4	
NH_4	Frequencies (obs.)	1469·7	1555·3	1638·6	1720·3	1803·1	1886·8	1971·5	2054·6
	,, (calc.)	1470·9	1554·3	1637·6	1720·9	1804·3	1887·6	1970·9	2054·3
	Differences .	+ 1·2	− 1·0	− 1·0	+ 0·6	+ 1·2	+ 0·8	− 0·6	− 0·3
	Intervals (obs.) .	85·6	83·3	81·7	82·8	83·7	84·7	83·1	
Rb	Frequencies (obs.)	—	1557·6	1640·0	1724·0	1806·0	1890·0	1973·8	2059·0
	,, (calc.)	—	1556·2	1639·7	1723·2	1806·7	1890·1	1973·6	2057·1
	Differences .	—	− 1·4	− 0·3	− 0·8	+ 0·6	+ 0·1	− 0·2	− 1·9
	Intervals (obs.) .	—	83·4	84·0	82·1	83·9	83·8	85·2	
Cs	Frequencies (obs.)	—	1562·3	1643·9	1727·4	1808·6	1891·1	1973·5	2056·3
	,, (calc.)	—	1562·0	1644·3	1726·6	1809·0	1891·3	1973·6	2055·9
	Differences .	—	− 0·3	+ 0·4	− 0·8	+ 0·4	+ 0·2	+ 0·1	− 0·4
	Intervals (obs.) .	—	81·6	83·5	81·2	82·5	82·4	82·8	

SERIES C.

		Group 1.	Group 2.	Group 3.	Group 4.	Group 5.	Group 6.	Group 7.	Group 8.
K	Frequencies (obs.)	—	1568·6	1652·5	1736·4	1819·3	1901·5	1984·4	2068·0
	,, (calc.)	—	1569·3	1652·4	1735·6	1818·9	1901·8	1984·9	2068·0
	Differences .	—	+ 0·7	− 0·1	− 0·8	− 0·6	+ 0·3	+ 0·5	0·0
	Intervals (obs.) .	—	83·9	83·9	82·9	82·2	82·9	83·6	
NH_4	Frequencies (obs.)	1489·9	1572·9	1655·3	1738·6	1820·7	1904·6	1987·6	2071·0
	,, (calc.)	1489·4	1572·4	1655·4	1738·4	1821·4	1904·4	1987·4	2070·4
	Differences .	− 0·5	− 0·5	+ 0·1	− 0·2	+ 0·7	− 0·2	− 0·2	− 0·6
	Intervals (obs.) .	83·0	82·4	83·3	82·1	83·9	83·0	83·4	
Rb	Frequencies (obs.)	—	1573·8	1658·3	1741·6	1822·8	1905·5	1989·1	2072·8
	,, (calc.)	—	1574·5	1657·5	1740·4	1823·4	1906·4	1989·3	2072·3
	Differences .	—	+ 0·7	− 0·8	− 1·2	+ 0·6	+ 0·9	+ 0·2	− 0·5
	Intervals (obs.) .	—	84·5	83·3	81·2	82·7	83·6	83·7	
Cs	Frequencies (obs.)	—	1578·5	1662·5	1745·4	1827·5	1910·4	1990·3	2075·0
	,, (calc.)	—	1579·6	1662·1	1744·6	1827·1	1909·6	1992·0	2074·6
	Differencies .	—	+ 1·1	− 0·4	− 0·8	− 0·4	− 0·8	+ 1·7	− 0·4
	Intervals (obs.) .	—	84 0	82·9	82·1	82·9	79·9	84·7	

SERIES D.

		Group 1.	Group 2.	Group 3.	Group 4.	Group 5.	Group 6.	Group 7.
K	Frequencies (obs.)	—	1586·6	1671·5	1754·9	1837·6	1920·1	2004·0
	,, (calc.)	—	1587·6	1670·9	1754·2	1837·5	1920·8	2004·1
	Differences .	—	+ 1·0	− 0·6	− 0·7	− 0·1	+ 0·7	+ 0·1
	Intervals (obs.) .	—	84·9	83·4	82·7	82·5	83·9	
NH_4	Frequencies (obs.)	1507·1	1589·6	1672·7	1755·7	1839·7	1923·2	2005·7
	,, (calc.)	1506·6	1589·8	1673·0	1756·2	1839·4	1922·6	2005·8
	Differences .	− 0·5	+ 0·2	+ 0·3	+ 0·5	− 0·3	− 0·6	+ 0·1
	Intervals (obs.) .	82·5	83·1	83·0	84·0	83·5	82·5	
Rb	Frequencies (obs.)	—	1592·2	1675·9	1758·7	1841·5	1925·0	2008·4
	,, (calc.)	—	1592·4	1675·6	1758·7	1841·9	1925·1	2008·2
	Differences .	—	+ 0·2	− 0·3	0·0	+ 0·4	+ 0·1	− 0·2
	Intervals (obs.) .	—	83·7	82·8	82·8	83·5	83·4	
Cs	Frequencies (obs.)	—	1590·1	1675·0	1757·9	1840·5	1923·6	2004·4
	,, (calc.)	—	1592·2	1675·0	1757·9	1840·7	1923·6	2006·4
	Differences .	—	+ 2·1	0·0	0·0	+ 0·2	0·0	+ 2·0
	Intervals (obs.) .	—	84·9	82·9	82·6	83·1	80·0	

TABLE LII.—*Continued.*

SERIES E.

		Group 1.	Group 2.	Group 3.	Group 4.	Group 5.	Group 6.	Group 7.
K	Frequencies (obs.)	—	1606·4	1689·5	1772·3	1855·3	1938·3	2021·7
	,, (calc.)	—	1606·4	1689·4	1772·4	1855·4	1938·4	2021·4
	Differences .	—	0·0	− 0·1	+ 0·1	+ 0·1	+ 0·1	− 0·3
	Intervals (obs.) .		—	83·1	82·8	83·0	83·0	83·4
NH_4	Frequencies (obs.)	1521·8	1604·9	1688·2	1772·3	1856·9	1940·5	2024·1
	,, (calc.)	1521·2	1605·0	1688·8	1772·6	1856·4	1940·2	2024·0
	Differences .	− 0·6	+ 0·1	+ 0·6	+ 0·3	− 0·5	− 0·3	− 0·1
	Intervals (obs.) .		83·1	83·3	84·1	84·6	83·6	83·6
Rb	Frequencies (obs.)	—	1611·3	1694·1	1777·8	1859·8	1943·5	2026·2
	,, (calc.)	—	1611·4	1694·1	1777·3	1860·3	1943·3	2026·2
	Differences .	—	+ 0·1	0·0	− 0·5	+ 0·5	− 0·2	0·0
	Intervals (obs.) .		—	82·8	83·7	82·0	83·7	82·7
Cs	Frequencies (obs.)	—	1608·0	1691·9	1775·9	1859·1	1942·7	2025·1
	,, (calc.)	—	1608·4	1691·9	1775·4	1858·9	1942·3	2025·8
	Differences .	—	+ 0·4	0·0	− 0·5	− 0·2	− 0·4	+ 0·7
	Intervals (obs.) .		—	83·9	84·0	83·2	83·6	82·4

The fairly regular increase in actual wave-numbers of the corresponding bands in passing from potassium to cæsium is clearly shown in Table LI. The constancy of this increase is well shown by the values given previously in Table L. of the centres of the band groups. Neglecting group 7 in which the bands are displaced by absorption in a manner presently to be described, the values of this increase are given in Table LIII.

TABLE LIII.

Group .	2	3	4	5	6
Increase .	5·4	5·1	5·3	5·2	5·1

Average increase from K to Cs, 5·2.

The average values of this increase for the individual radicals are given in Table LIV.

TABLE LIV.

K to NH_4 . .	1·6
NH_4 to Rb . .	2·7
Rb to Cs . . .	0·9

and it will be noted that NH_4 lies between K and Rb, which agrees with the observations of Tutton.[1]

Turning now to the effect of low temperature, the fluorescence spectra of the double uranyl chlorides undergo resolution. The following excerpt from Nichols and Howes' monograph will explain

[1] *Crystalline Structure and Chemical Constitution.* Macmillan, London, 1916.

the relations between the fluorescence spectra at 20° and — 185°. As the temperature is decreased the bands are gradually resolved into doublets. One component of each doublet becomes rapidly more intense, whilst the other frequently becomes more indistinct, and sometimes disappears. The general effect is that of a shift of each band towards the violet amounting to about one-third of the distance between two of the original bands. Each band at 20° may be regarded as an unresolved doublet, of which, in general, the member of longer wave-length is relatively so much stronger that its position determines approximately the location of the crest of the composite band. The effect of cooling is to resolve this doublet into separately distinguishable bands, and at the same time to cause a subsidence of the stronger and an increase of the weaker member.

The member of the shorter wave-length usually becomes dominant at low temperatures, and in so far as this occurs the arrangement of the spectrum appears to be undisturbed, but shifted towards the violet by an amount representing the width of the doublet. There are, however, certain exceptions to this rule, so that the relation of the resolved spectrum to that at + 20° is not so simple as the above description would imply. The appearance of the group, if this be its real structure (*i.e.* a set of nearly equidistant doublets, the distance between the members of all the doublets being nearly the same), would then be shown as in Fig. 71.

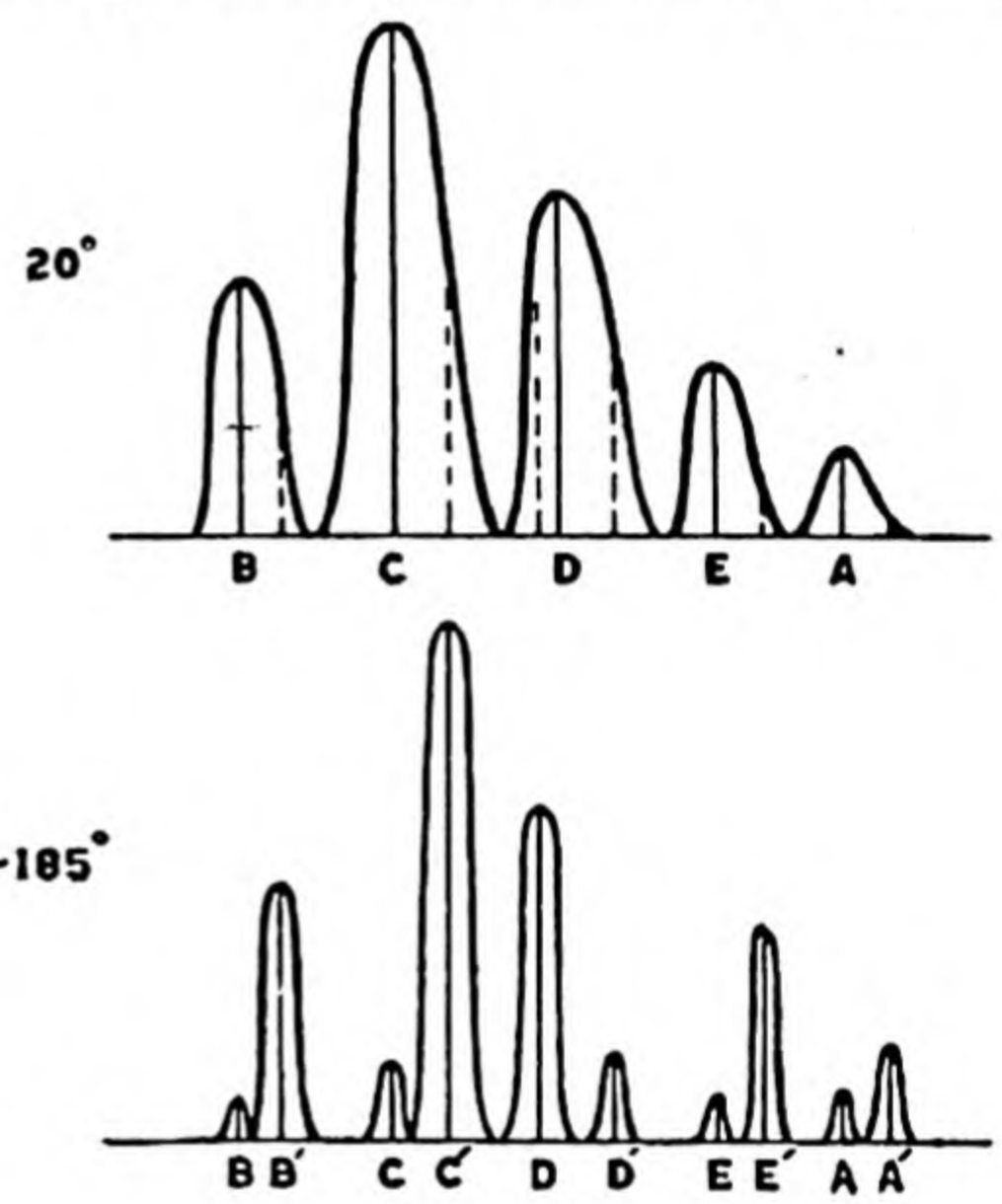


FIG. 71.

At + 20°, B′, C′, E′, and A′ are entirely concealed by the overlapping of the bands. At — 185°, B, C, D′, E, and A may or may not be visible, according to their intensity or the completeness of the resolution, which, in fact, varies greatly in different parts of the spectrum.

It will be noticed that in the lower diagram in Fig. 71, D and not D′ is the dominant component. This is a condition which obtains in the ammonium chloride, with the result that C′ and D, which appear to have replaced the strong C and D bands of the spectrum of + 20°, are near together, D and E′ far apart, and the symmetry of the group is impaired. Similar complications occur likewise in the spectra of the other double chlorides.

To illustrate the application of this assumption, the spectrum of the ammonium uranyl chloride has been mapped in the manner shown in Fig. 72, in which the fluorescent bands of the eight groups as they

occur at — 185° are shown in their relation to a hypothetical grouping given at the head of the diagram. This grouping consists of the set of imagined doublets of which the spectrum at — 20° is supposed to be made up. The spacing for each doublet is that determined from the observed average shift on cooling and the relative divergence from this arrangement is shown for all the bands of each group.

A scrutiny of the fluorescence spectrum at — 185°, group by group, by means of this diagram, affords very satisfactory confirmation of this hypothesis concerning the apparent shift. It is obvious:

1. That not all the components B, C, D, E, and A will necessarily be visible in every group of the resolved spectrum.

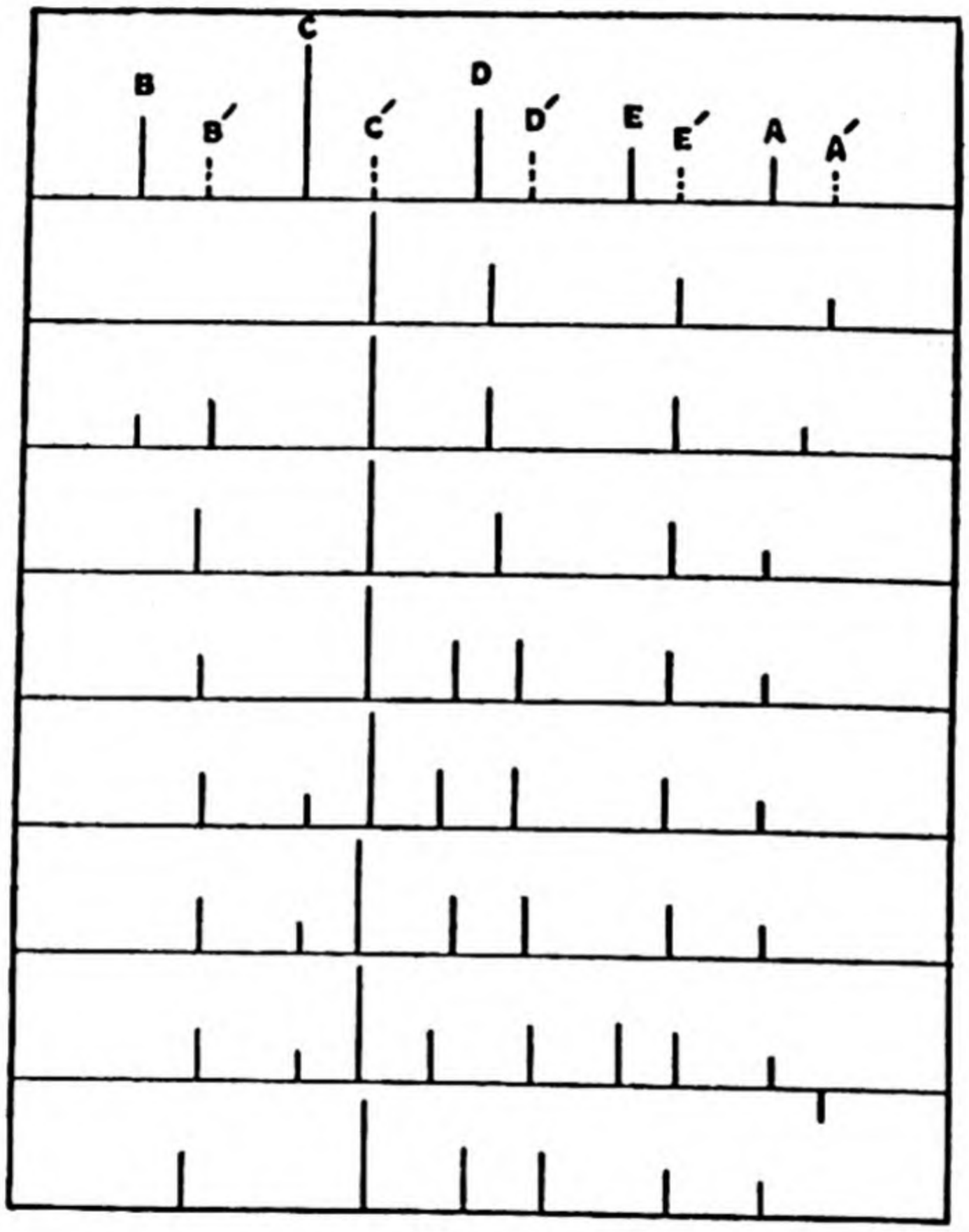


FIG. 72.

2. That lack of resolution in any region may give the appearance of a single band with intermediate crest in place of the doublet.

3. That the position of crests of the unresolved doublets at + 20° will not necessarily coincide exactly with that of either component.

Bearing these points in mind, it will be seen that were resolution complete, all the observed bands of the spectrum at — 185° would probably fall into the system proposed above.

We may imagine that the difference between the resolution of the bands C and D, for example, as seen in Fig. 73, is produced by changes in the unresolved doublets at + 20° when the temperature is reduced to — 185°, of the kind indicated in Fig. 74. The doublet CC′ forms

a single band with crest nearly coincident with C at + 20°, and this owing to the subsidence of C and growth of C′ takes the resolved form shown at — 185°. In the case of D, however, the unresolved band has an intermediate crest at D, but is really composed of overlapping components D′ and D″ which are separately visible at — 185°.

The wave-lengths and frequencies of the bands in the resolved spectra of the four double chlorides, as observed when excited at the temperature of liquid air, are given in Table LV.

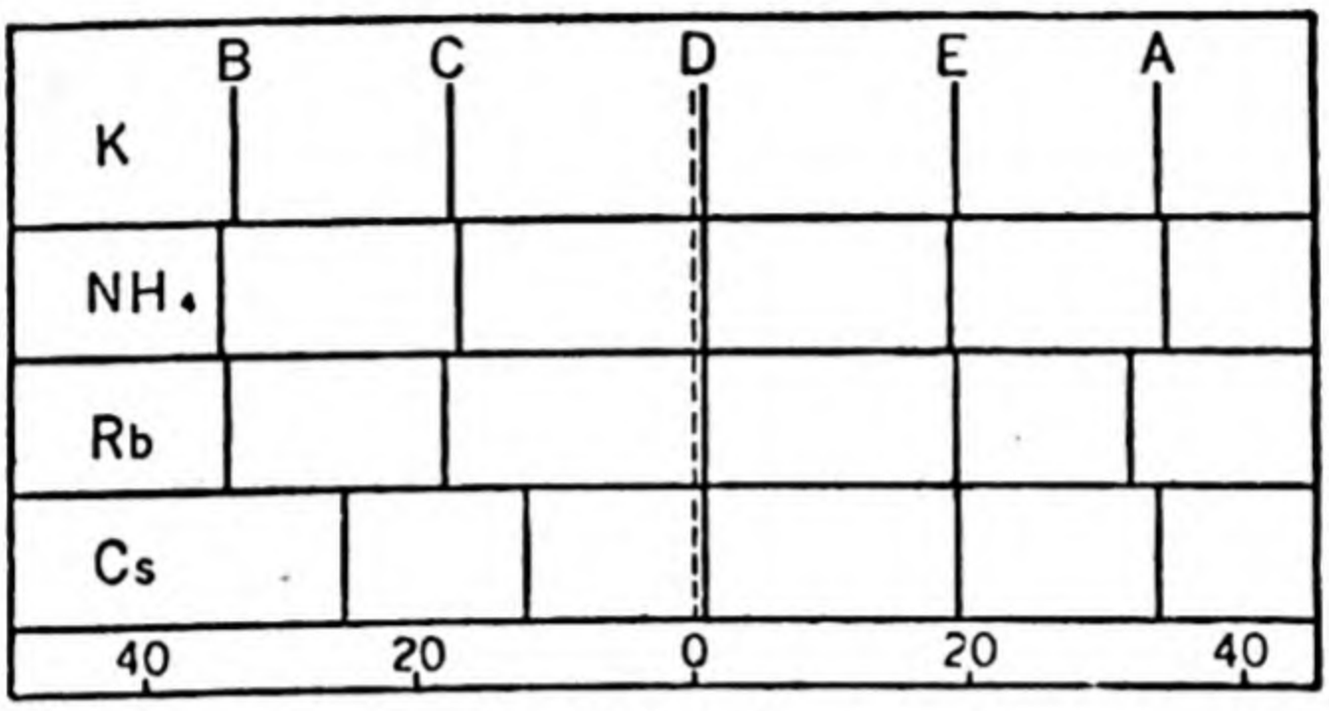


FIG. 73.

The nomenclature used in this and other tables is chosen to indicate, as far as possible, the relation of the bands at — 185° to those at + 20°. Thus B_1 and B_2, etc., denote components of B, etc., which have been rendered visible by the resolution effected by cooling.

The explanation offered above to account for the relation between the spectra at + 20° and at — 185°, and which was illustrated in the case of the ammonium uranyl chloride (see Fig. 72), was confirmed by observations upon the spectrum of that salt at intermediate temperatures. It was thus possible to watch the gradual appearance of the components characteristic of the spectrum at low temperatures and the simultaneous fading away of those dominant at + 20°. The same explanation applies equally well to the potassium and rubidium double chlorides. In the case of cæsium uranyl chloride the relations are complicated by the further resolution of these components, so that the connection with the original complexes is less easily traced.

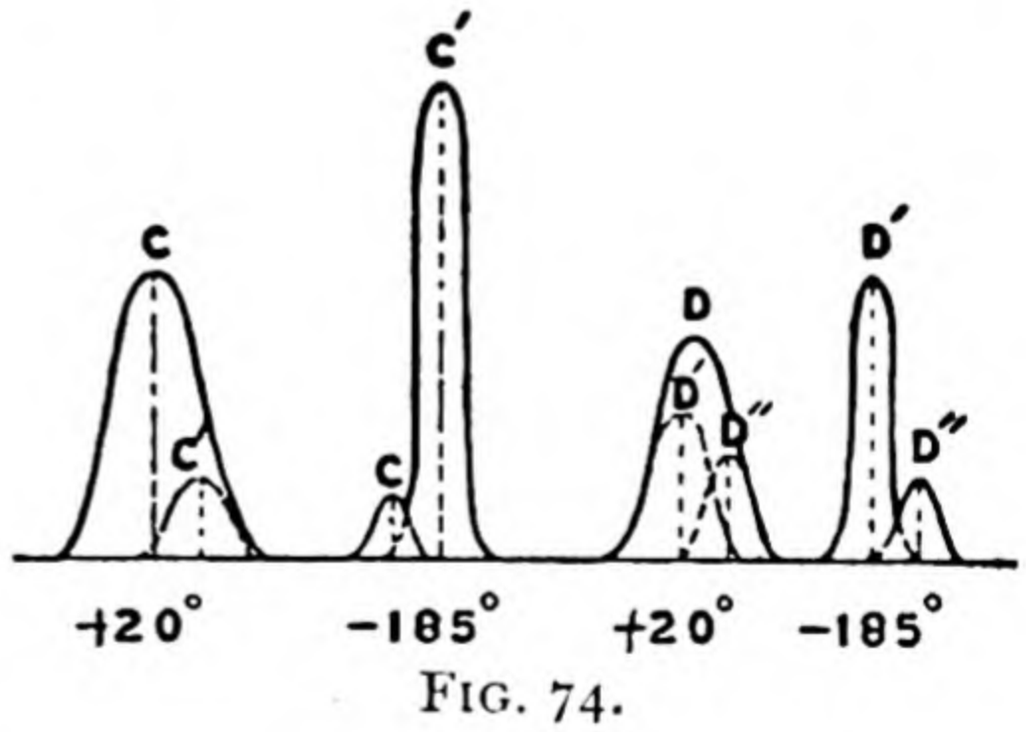


FIG. 74.

To indicate the general character of these resolutions and the apparent temperature shift which results therefrom, the positions of the bands of group 6 at — 185° are plotted for all four chlorides in Fig. 75. Intensities of the — 185° bands are indicated roughly by the height of the lines. The corresponding crests of the bands at + 20°

TABLE LV.

Group and series.	Potassium uranyl chloride.		Ammonium uranyl chloride.		Rubidium uranyl chloride.		Cæsium uranyl chloride.	
	λ.	$1/\lambda \times 10^3$.	λ.	$1/\lambda \times 10^3$.	λ.	$1/\lambda \times 10^3$.	λ.	$1/\lambda \times 10^3$.
2 B_2	—	—	0·6398	1563·0	—	—	—	—
2 C_2	—	—	0·6630	1579·8	—	—	—	—
2 D_2	—	—	0·6283	1591·5	—	—	—	—
2 F_2''	—	—	0·6207	1611·0	—	—	—	—
3 B_1	—	—	0·6110	1636·7	—	—	—	—
3 B_2	—	—	0·6079	1645·0	—	—	0·6056	1651·3
3 C_2	0·6035	1657·0	0·6016	1662·1	0·6018	1661·7	0·5991	1669·2
3 D_1	0·6006	1665·0	—	—	0·5990	1669·4	0·5964	1676·7
3 D_2	—	—	0·5968	1675·6	—	—	—	—
3 E_2''	—	—	0·5899	1695·0	—	—	—	—
4 B_2	0·5803	1723·2	0·5791	1726·9	—	—	0·5764	1734·9
4 C_1	—	—	—	—	—	—	0·5721	1747·9
4 C_2	0·5752	1738·4	0·5733	1744·4	0·5731	1745·0	0·5705	1752·7
4 D_1	0·5724	1747·0	0·5704	1753·1	0·5703	1753·4	0·5684	1759·4
4 D_2	—	—	0·5677	1761·4	—	—	0·5652	1769·3
4 E_2'	0·5641	1772·7	—	—	—	—	—	—
4 E_2''	—	—	0·5624	1778·1	—	—	—	—
4 A_1	0·5603	1784·6	0·5595	1787·3	—	—	—	—
4 A_2	—	—	—	—	0·5573	1794·5	0·5564	1797·2
5 B_1	0·5569	1795·8	—	—	0·5546	1803·1	0·5526	1809·5
5 B_2	0·5542	1804·4	0·5524	1810·4	0·5520	1811·5	0·5500	1818·1
5 C_1	0·5508	1815·5	0·5493	1820·5	0·5489	1821·9	0·5464	1830·2
5 C_2	0·5489	1821·7	0·5471	1827·7	0·5471	1827·8	0·5452	1834·1
5 D_1'	—	—	—	—	—	—	0·5440	1838·2
5 D_1	0·5461	1831·0	0·5445	1836·7	0·5444	1836·9	0·5427	1842·5
5 D_2'	—	—	—	—	—	—	0·5412	1847·7
5 D_2	0·5437	1839·4	0·5420	1845·1	0·5419	1845·2	0·5395	1853·7
5 E_2'	0·5389	1855·7	0·5379	1859·0	—	—	—	—
5 E_2''	—	—	0·5370	1862·0	—	—	0·5358	1866·4
5 A_1	0·5354	1867·6	0·5345	1870·8	—	—	—	—
5 A_2	—	—	—	—	0·5326	1877·7	0·5318	1880·4
6 B_1	0·5321	1879·5	—	—	0·5300	1886·8	0·5286	1891·8
6 B_2	0·5297	1888·0	0·5279	1894·4	0·5277	1895·0	0·5260	1901·1
6 B_3	0·5279	1894·3	—	—	—	—	—	—
6 C_1	0·5262	1900·4	0·5250	1904·8	0·5247	1905·9	0·5223	1914·6
6 C_2	0·5250	1904·6	0·5234	1910·6	0·5231	1911·7	0·5214	1918·0
6 D_1'	—	—	—	—	—	—	0·5201	1922·7
6 D_1	0·5226	1913·5	0·5206	1921·0	0·5207	1920·3	0·5191	1926·3
6 D_2'	—	—	—	—	—	—	0·5179	1930·9
6 D_2	0·5200	1922·9	0·5184	1929·2	0·5182	1929·9	0·5163	1937·9
6 E_2'	0·5155	1939·9	0·5149	1941·9	—	—	0·5137	1946·8
6 E_2''	—	—	0·5141	1945·0	—	—	0·5127	1950·4
6 A_1	0·5124	1951·6	0·5118	1953·7	0·5107	1957·9	—	—
6 A_2	—	—	—	—	0·5098	1961·6	0·5092	1963·9

TABLE LV.—*Continued.*

Group and series.	Potassium uranyl chloride.		Ammonium uranyl chloride.		Rubidium uranyl chloride.		Cæsium uranyl chloride.	
	λ.	$1/\lambda \times 10^3$.	λ.	$1/\lambda \times 10^3$.	λ.	$1/\lambda \times 10^3$.	λ.	$1/\lambda \times 10^3$.
7 B_1	0·5092	1963·9	0·5080	1968·7	0 5073	1971·4	0·5059	1976·5
7 B_2	0·5070	1972·3	0·5056	1977·9	0 5054	1978·6	0 5038	1984·9
7 B_3	0·5056	1977·8	—	—	—	—	—	—
7 C_1	—	—	0·5028	1988·7	—	—	0·5006	1997·6
7 C_2	0·5031	1987·6	0·5018	1992·7	0·5018	1993·0	—	—
7 D_1	0·5007	1997·2	0 4989	2004·5	0·4991	2003·7	0·4979	2008·5
7 D_2'	—	—	—	—	—	—	0·4963	2014·9
7 D_2	0·4982	2007·4	0·4967	2013·4	0·4967	2013·2	0·4950	2020·2
7 E_1	0·4956	2017·8	—	—	0·4938	2025·1	—	—
7 E_2'	—	—	0·4940	2024·1	—	—	0.4926	2030·0
7 E_2''	—	—	—	—	—	—	0·4918	2033·3
7 A_1'	0·4930	2028·4	—	—	0·4917	2033·8	—	—
7 A_1	0·4916	2034·2	—	—	0·4902	2040·0	—	—
7 A_2	0·4904	2039·2	—	—	—	—	—	—
8 B_1	—	—	—	—	—	—	0·4857	2058·9

are represented by dotted lines. Group 6 was selected because it offers better examples of the further breaking-up of the components and of other phases of the process of resolution than do groups towards the red in which the resolution is progressively less complete.

Two questions which were left undetermined in the study of the spectra at + 20° may be regarded as settled by these measurements of the bands at − 185°:—

1. That the intervals are not the same for all series in a given spectrum is clearly established. For example, the components C_1, C_2 which take the place of the C bands in all four spectra, have distinctly different intervals, *i.e.* 84·00 for C_1 and 82·75 for C_2. It is noteworthy that C_2, which becomes the crest of the group in place of C_1, also has the small interval. It might be questioned whether these so-called components are not merely accidental neighbours rather than products of the same vibrating system, but for the fact that they are present in all the spectra and have very nearly, if not precisely, the same relative positions to each other in all.

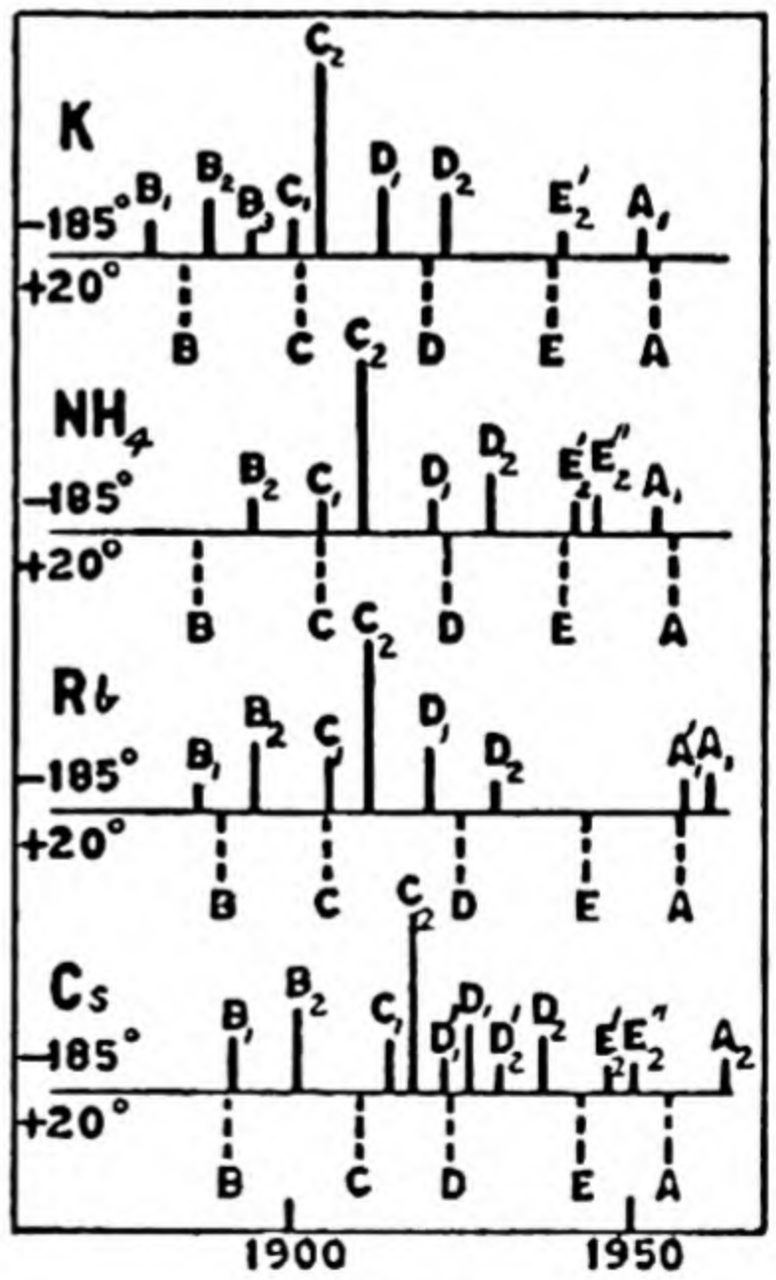


FIG. 75.

2. The average interval of all series in the spectrum of the cæsium chloride (82·80) at + 20°, which causes the notable displacement of the bands of that substance, becomes 83·44 when we take the average of the intervals of the bands at — 185°. That is to say, it is, within the errors of observation, the same as the general average for the other salts. On the basis of the measurements at low temperatures (see Table LV.), we must conclude that the four double chlorides have approximately the same average frequency interval.

The averages given in Table LVI. are obtained from the wave-numbers of all the fluorescence bands observed in the spectra of the four double chlorides when excited at the temperature of liquid air, and given in Table LV. As in the corresponding table for + 20°, the arrangement is by series.

TABLE LVI.

Series.	K.	NH_4.	Rb.	Cs.	Average.
B_1 . .	83·9	83·0	84·2	83·0	83·53
B_2 . .	83·1	83·2	83·6	83·4	83·33
B_3 . .	83·5	—	—	—	—
C_1 . .	84·9	84·1	84·0	83·7	84·18
C_2 . .	82·7	82·7	82·9	82·8	82·78
D_1 . .	83·1	83·8	83·6	83·1	83·40
D_1' . .	—	—	—	84·5	—
D_2 . .	84·1	84·2	84·0	83·6	83·98
D_2' . .	—	—	—	83·6	—
E_2' . .	83·6	82·5	—	83·2	83·10
E_2'' . .	—	83·3	—	83·5	83·40
A_1 . .	83·3	83·1	82·1	—	82·83
A_2 . .	—	—	83·6	83·4	83·50
Average .	83·58	83·32	83·50	83·44	—

Up to the present brief reference only has been made to the absorption spectra of the uranyl salts. Whilst it might possibly be considered that this side of the phenomenon should be postponed until the whole problem of absorption spectra is dealt with in Vol. IV., the intimate relationship which has been proved to exist between the absorption and fluorescence of the uranyl salts renders it necessary to discuss both phenomena at one and the same time.

The absorption spectra of the double uranyl chlorides have been studied in great detail at 20° and — 185° by Nichols and his colleagues, who found the complete mapping of these spectra to be difficult. The measurements were made both visually and photographically, but the latter method does not extend the range far into the ultra-violet on account of the greatly increasing opacity. A great variety of light filters were employed and the thickness of the absorbing salt was varied as much as possible. By using considerable thicknesses of the substances, it was found possible to extend considerably the absorp-

tion spectrum towards the red beyond the limits previously observed. To a certain extent the crystal acts as a screen to absorb the blue light which excites the fluorescence, but it was found necessary to interpose orange or yellow screens in order to eliminate fluorescence in a region where ordinarily it is a maximum. It was hoped that monochromatic light could be used, thus preventing all fluorescence, but it was found that such light could not be made of sufficient intensity to study the weaker absorption lines.

In Fig. 76 is represented a portion of the fluorescence and absorption spectra of the four double chlorides at 20°. The fluorescence bands are indicated by lines above the horizontal line, the well-known absorption bands by dotted lines below the horizontal, whilst the new absorption bands are indicated by full lines below the horizontal. The absorption bands belong to two distinct groups :—

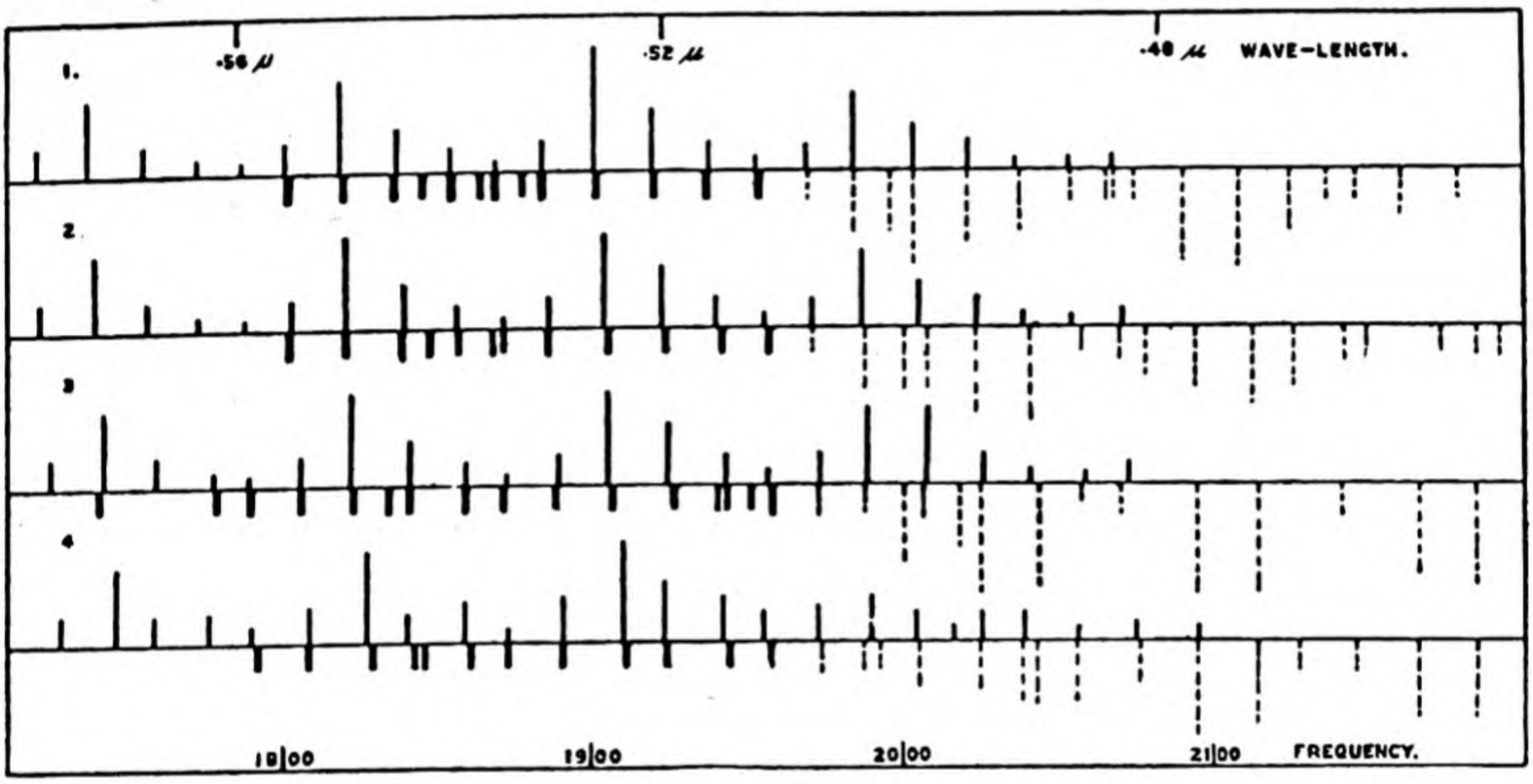


FIG. 76.

1. Most of them are reversals of fluorescence bands, as may be seen more clearly from Table LVII., which contains the measurements of both sets of bands as exhibited by the four salts. These bands do not form a continuation of the absorption series lying further towards the violet, which have the constant wave-number interval of about 71. In all four salts every fluorescent band of groups 5 and 6 has its corresponding absorption band, and this is also true for some of the bands in group 4. Nichols and Howes believe that, provided the right conditions were obtained, this would be true of every fluorescent band.

2. The remaining bands given in Table LVII. are normal absorption bands which belong to the series with constant interval of about 71.

It is very important to note that the new absorption bands, that is to say, the bands of group 1, disappear at the temperature of liquid air. Nichols and Howes consider, however, that their existence at

TABLE LVII.

Potassium uranyl chloride.				Ammonium uranyl chloride.			
Absorption.	Fluorescence.	Fluorescence series.	Absorption series.	Absorption.	Fluorescence.	Fluorescence series.	Absorption series.
1802·1	1801·4	B	—	1802·5	1803·1	B	—
1820·2	1819·3	C	—	1820·8	1820·7	C	—
1836·5	1837·6	D	—	1838·9	1839·7	D	—
1846·0	—	—	*c*	1848·8	—	—	*c*
1855·3	1855·3	E	—	1857·8	1856·9	E	—
1865·0	—	—	*d*	1869 2	—	—	*d''*
1869·4	1869·6	A	—	1871·8	1871·8	A	—
1879·0	—	—	*e*	1886·5	1886·8	B	—
1885·1	1884·7	B	—	1906·2	1904·6	C	—
1902·2	1901·5	C	—	1924·2	1923·2	D	—
1920·9	1920·1	D	—	1942·3	1940·5	E	—
1937·6	1938·3	E	—	1957·4	1956·3	A	—
1954·7	1953·5	A	—				

Rubidium uranyl chloride.				Cæsium uranyl chloride.			
Absorption.	Fluorescence.	Fluorescence series.	Absorption series.	Absorption.	Fluorescence.	Fluorescence series.	Absorption series.
1740·0	1741·6	C	—	1791·5	1789·7	A	—
1778·7	1777·8	E	—	1808·0	1808·6	B	—
1789·5	1789·4	A	—	1829·2	1827·5	C	—
1806·1	1806·1	B	—	1843·0	1840·5	D	—
1823·2	1822·8	C	—	1846·4	—	—	—
1834·9	—	—	*b*	1861·2	1859·1	E	*β*
1841·6	1841·5	D	—	1873·0	1873·1	A	—
1859·8	1859·8	E	—	1890·7	1891·1	B	—
1872·0	1873·1	A	—	1911·1	1910·4	C	—
1889·0	1890·0	B	—	1923·8	1923·6	D	—
1907·2	1905·5	C	—	1944·4	1942·7	E	—
1926·7	1925·0	D	—	1957·8	1955·7	A	—
1941·7 ?	—	—	*d*				
1944·0	1943·5	E	—				
1952·0 ?	—	—	*e* ?				
1958·7	1957·1	A	—				

the low temperature is probable, and that the experimental conditions were not suitable for their appearance. On the other hand, it is possible that another explanation may be found in the fact that the molecules of the uranyl salts are in a different energy state at the low temperature, and that they no longer possess the power of absorbing radiations of those frequencies.

It is not possible to give a full description of the absorption spectra of the uranyl salts at — 185°, which are described in great detail by Nichols and Howes in their memoir. It may be mentioned that the general effect of cooling is a resolution into doublets, and in some cases

still greater resolution. Every low temperature absorption band belongs to a series of constant wave-number difference, whatever its position or degree of resolution. The absorption spectrum at — 185° is of greater extent than the fluorescence spectrum, and the effect of cooling is such that the absorption, considered as a unit, becomes narrower, this being more marked on the side towards the red.

One of the most interesting phenomena observed by Nichols and

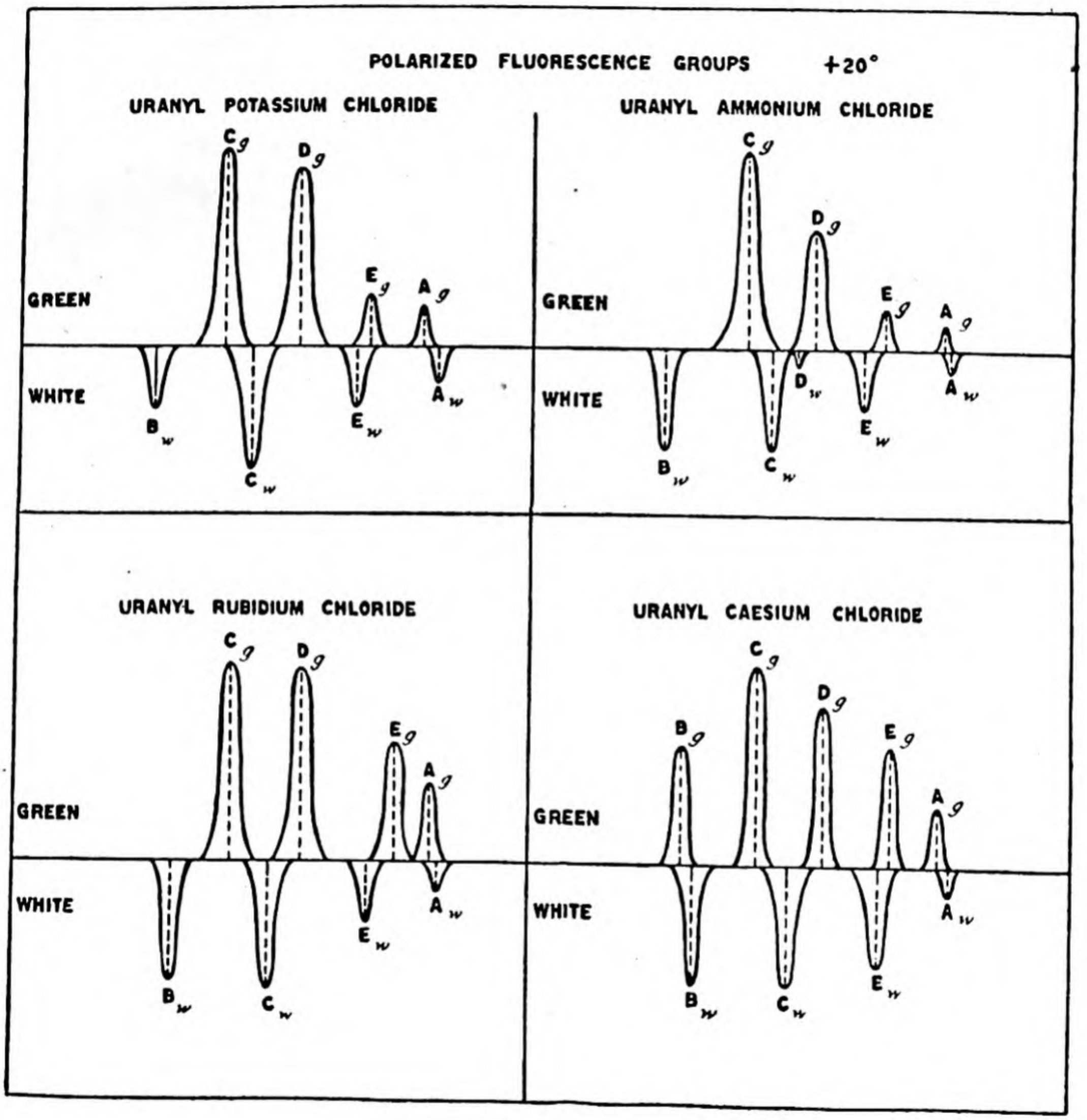


FIG. 77.

his colleagues in the course of their investigations was the polarised spectra, both fluorescence and absorption. The polarisation of fluorescence spectra, as given by crystals, has long been known, but in the ordinary case of a single broad fluorescence band the most that can be done is the determination of the direction of the vibration and the proportion of the polarised light. The crystals of the uranyl salts, and in particular the double chlorides, offer much more favourable opportunities for the investigation of this phenomenon. Well-formed

crystals of these salts show a marked pleochromism. When viewed through a Nicol prism, their colour changes from yellow-green to very pale yellowish-white when the Nicol is rotated through 90°. These colour changes are associated with striking and significant variations in the fluoresence and absorption spectra. The double uranyl chlorides were examined in detail at 20° and at — 185°. As has previously been described, the single bands are resolved into doublets at — 185° and these are polarised, the vibration planes of the two

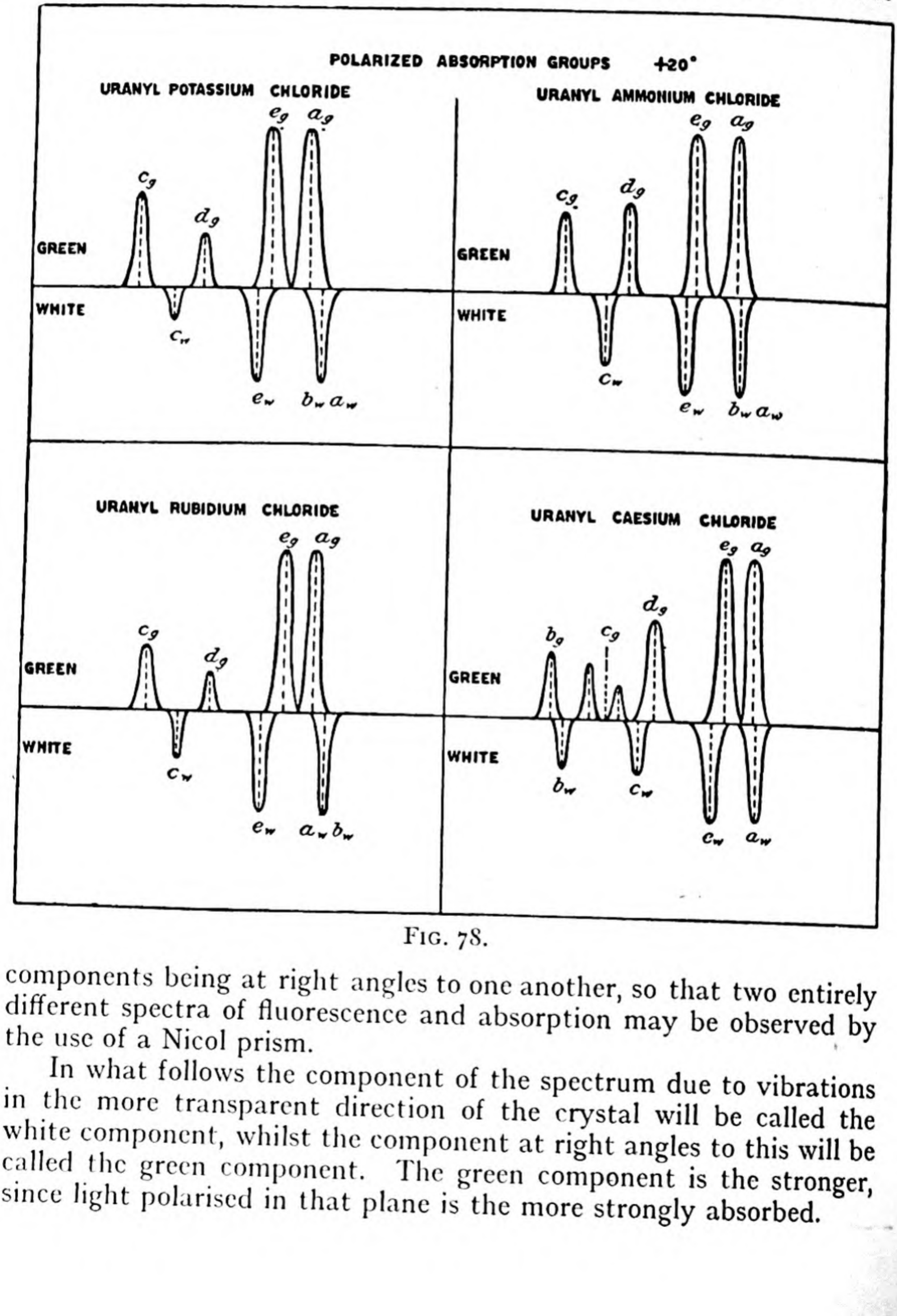


FIG. 78.

components being at right angles to one another, so that two entirely different spectra of fluorescence and absorption may be observed by the use of a Nicol prism.

In what follows the component of the spectrum due to vibrations in the more transparent direction of the crystal will be called the white component, whilst the component at right angles to this will be called the green component. The green component is the stronger, since light polarised in that plane is the more strongly absorbed.

Provided that the crystals are correctly mounted, two polarised fluorescence and two absorption spectra are visible, and these spectra are not influenced in any way, whether the exciting light is unpolarised or polarised, or is polarised in any direction. As we have already seen, the fluorescence spectra of the double chlorides are resolved at 20° into six or seven groups of five bands each, and consequently we should expect to find two polarised fluorescence spectra with six or seven groups of five bands each. This is not, however, exactly the

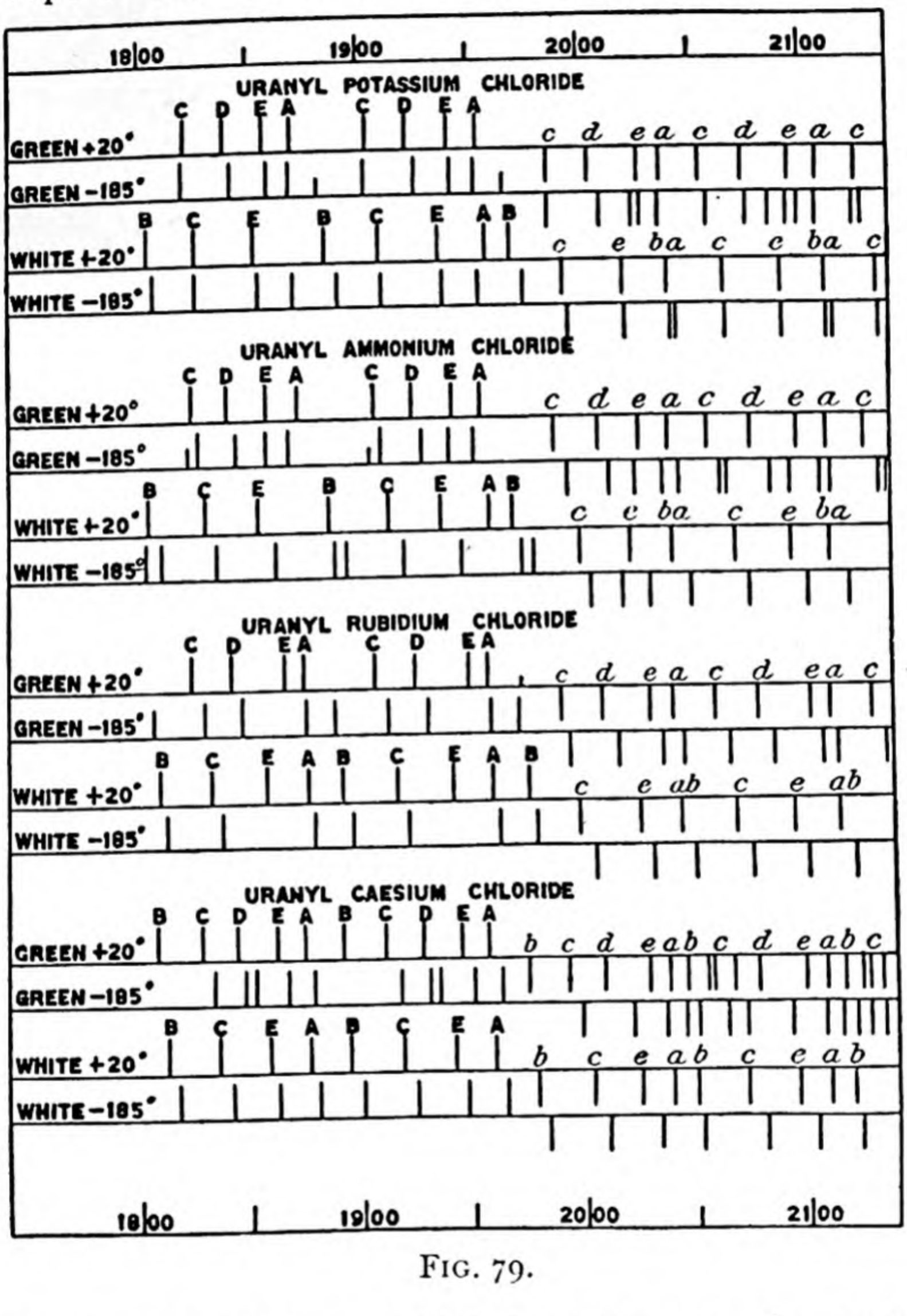


FIG. 79.

case, as is shown in Fig. 77, which is a diagram of a typical fluorescence band group. In this diagram the green polarised components are drawn above, and the white polarisation components below the horizontal line. It will be noticed that, except in the somewhat doubtful case of the ammonium salt, the D band has no white polarised component, and this is true of all the groups.

In Fig. 78 is shown a diagram of a typical group of absorption bands.

At — 185° the polarised fluorescence and absorption spectra corresponded to those already described for the non-polarised spectra at that temperature as regards resolution and strengthening of the weaker component and weakening of the stronger component, with the result that certain shifts occurred in their position. Just as in the case of the spectra at 20°, so at — 185° the D bands only occur in the green component and the B bands chiefly in the white component. In Fig. 79 is given a map of the contiguous fluorescence and absorption groups, as observed at the two temperatures. As previously, the absorption bands are represented by lines below the horizontal line.

As regards the homologous series of bands with constant wave-number intervals, these are set forth in Table LVIII.

TABLE LVIII.

AVERAGE WAVE-NUMBER INTERVALS + 20° C.

Fluorescence Series.

Green component.					White component.				
Series.	K.	NH_4.	Rb.	Cs.	Series.	K.	NH_4.	Rb.	Cs.
B .	—	—	—	82·9	B .	83·0	83·4	83·6	82·9
C .	81·9	82·8	82·2	82·6	C .	82·1	82·9	83·3	82·8
D .	83·0	83·5	83·1	83·3					
E .	83·2	83·3	83·5	83·3	E .	83·5	83·1	83·5	83·1
A .	83·4	83·8	83·2	82·9	A .	—	—	82·9	82·4
Absorption Series.									
b .	—	—	—	70·5	*b* .	71·5	71·3	70·4	70·8
c .	71·3	70·7	71·2	70·6	*c* .	71·3	70·3	70·0	70·5
d .	71·1	70·5	70·2	70·5					
e .	70·8	70·8	71·7	71·0	*e* .	70·4	71·7	70·8	70·4
a .	70·7	71·5	71·1	70·8	*a* .	71·5	71·3	70·4	71·4

AVERAGE WAVE-NUMBER INTERVALS — 185° C.

Fluorescence Series.

Green component.					White component.				
Series.	K.	NH_4.	Rb.	Cs.	Series.	K.	NH_4.	Rb.	Cs.
B .	84·0	—	83·4	—	B .	84·1	84·1	83·2	83·6
C .	82·5	83·4	82·6	82·2	C .	84·8	84·4	83·9	83·3
D .	83·7	84·4	83·9	83·3					
E .	83·3	83·2	—	83·6	E .	83·0	—	—	83·1
A .	84·1	84·4	84·1	84·1	A .	84·0	—	83·1	84·1
Absorption Series.									
b .	—	—	70·9	70·5	*b* .	71·3	71·3	70·8	70·6
c .	71·5	70·9	70·7	70·8	*c* .	69·8	70·6	70·3	70·7
d .	70·3	71·1	71·3	71·4					
e .	71·8	71·5	—	71·0	*e* .	71·4	70·7	71·1	70·9
a .	71·0	70·9	70·6	71·1	*a* .	70·4	—	—	70·6

AVERAGE WAVE-NUMBER INTERVALS + 20° C. AND 185° C.

General Averages of Intervals (by Salts).

Fluorescence.

	NH_4.	K.	Rb.	Cs.
Green + 20° and − 185° . .	83·60	83·25	83·25	83·19
White + 20° and − 185° . .	83·78	83·43	83·42	83·16
All fluorescence .	83·69	83·34	83·33	83·17

Absorption.

Green + 20° and − 185° . .	70·99	71·07	70·96	70·74
White + 20° and − 185° . .	71·02	70·96	70·55	70·70
All absorption .	71·00	71·01	70·75	70·72

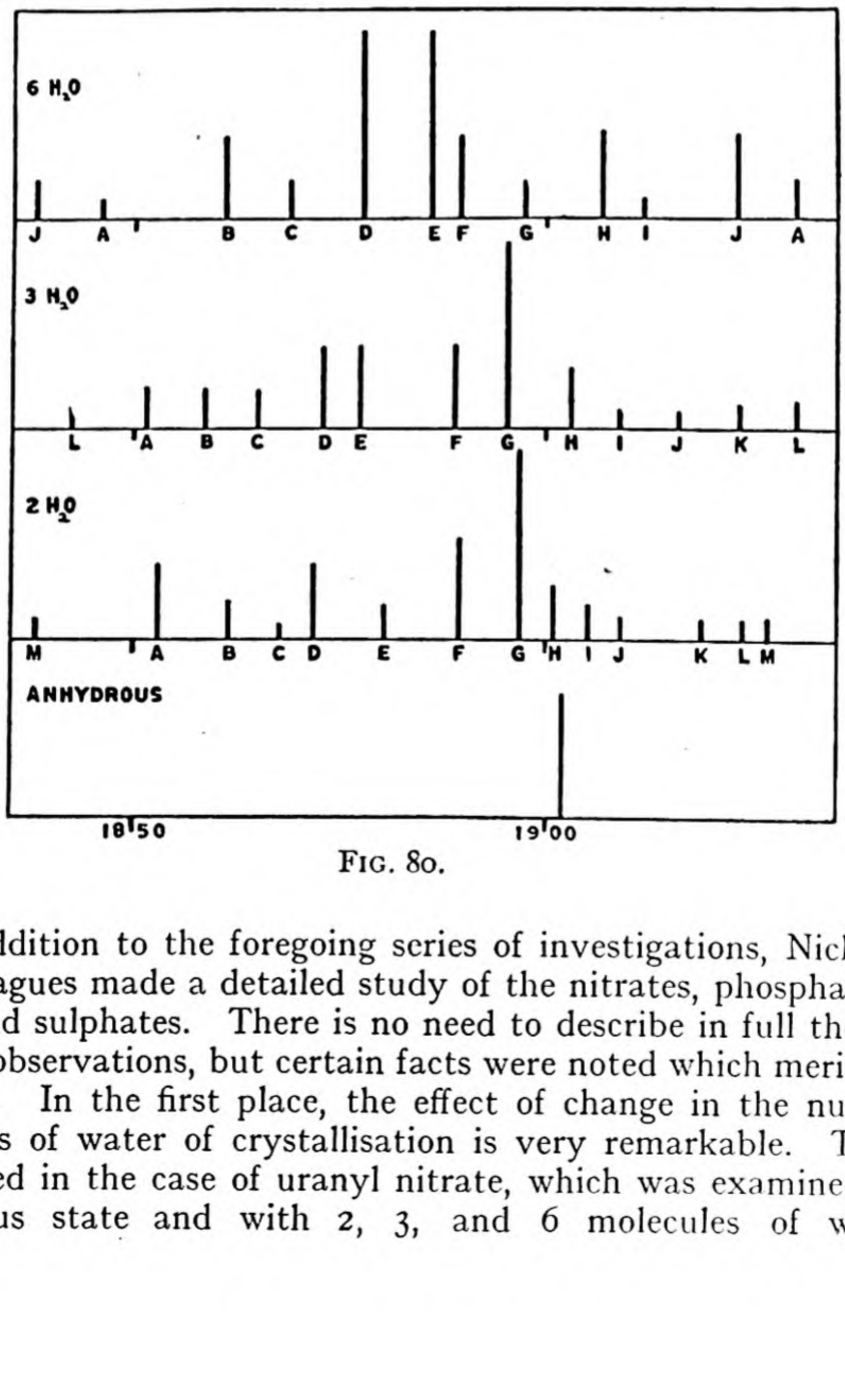


FIG. 80.

In addition to the foregoing series of investigations, Nichols and his colleagues made a detailed study of the nitrates, phosphates, acetates, and sulphates. There is no need to describe in full the results of their observations, but certain facts were noted which merit special mention. In the first place, the effect of change in the number of molecules of water of crystallisation is very remarkable. This was first noted in the case of uranyl nitrate, which was examined in the anhydrous state and with 2, 3, and 6 molecules of water of

crystallisation. A single band group from the spectra of each of the four salts as observed at — 185° is shown in Fig. 80, from which can at once be seen the marked differences between them. Although the homologous series of constant wave-number difference exist as in the case of all these uranyl spectra, yet it will be seen at once that the distribution of the individual bands within the group is very different in the spectra of the three hydrates. Then, again, it will be noticed that the distribution of intensity within the groups is markedly different in the case of the hexahydrate. These differences in the spectra are very significant, and they are fully as great as those between the spectra of two different uranyl salts. It may also be noted that, although the wave-number differences are constant for all the homologous series of bands for each of the four nitrates, this difference increases as the amount of water of crystallisation decreases. For the hexahydrate the constant difference is 86·0, for the trihydrate 86·8, for the dihydrate 88·1, and for the anhydrous salt it is 88·5. Nichols and his colleagues, basing their opinion on their results of the double uranyl nitrates, as well as on uranyl nitrate itself, conclude that a difference in crystalline form has an important influence upon the character of the fluorescence and absorption spectra of the uranyl salts.

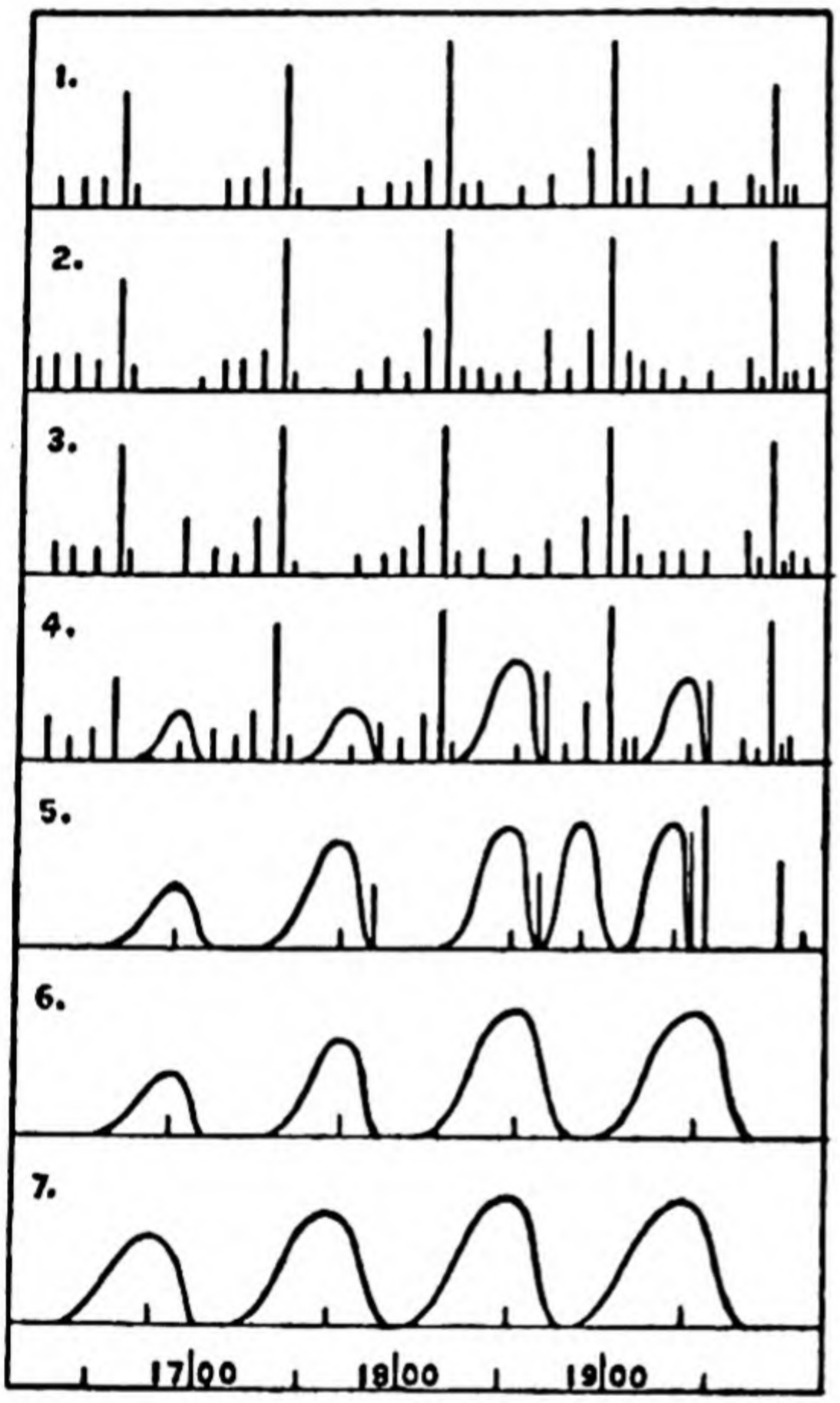


FIG. 81

That crystalline structure is a most important factor has also been established by the investigation on the uranyl phosphates, in the course of which it was found that the banded fluorescence spectra as observed with solid solutions at 20° are not resolved into groups of narrow bands at — 185°. This is well indicated by the seven spectra shown in Fig. 81, which are those given at — 185° by the following substances :—

1. A mixture of uranyl phosphate and sodium phosphate in the proportion of 4 molecules of HUO_2PO_4, $3\frac{1}{2}H_2O$, to 1 molecule of Na_2HPO_4.
2. A similar mixture in the proportion 2 : 1.
3. A similar mixture in the proportion 1 : 1.
4. A mixture of 1 molecule H_3PO_4, 2 molecules HUO_2PO_4, and

1 molecule Na_2HPO_4. This was a powder similar to preparations 1, 2, and 3.

5. A mixture of 1 molecule H_3PO_4, 1 molecule HUO_2PO_4 and 2 molecules Na_2HPO_4; when dried this contained much free sodium phosphate.

6. A mixture of 2 molecules H_3PO_4, 1 molecule HUO_2PO_4 and 1 molecule Na_2HPO_4. This remained syrupy at room temperature and appeared to be vitreous at — 185°.

7. A solution of uranyl phosphate in a considerable excess of syrupy phosphoric acid. This gave a glass-like mass even at 20°.

Similarly, the solid solution of uranyl phosphate in microcosmic salt yields a narrowing and a shift of the fluorescence bands on cooling, but no resolution. It seems probable that the dependence of resolution by cooling upon the existence of crystalline structure applies in general to the fluorescence of the uranyl salts.

In concluding this account of the work of Nichols and his colleagues on the fluorescence of the uranyl salts, one or two of their observations may be emphasised as being of special importance. In the first place, the proof they give of the fact that the associated group of wave-numbers in the fluorescence band is a single unit, which appears as a whole when the excitation is caused by one single absorption line or all the associated lines in the absorption band group, may be mentioned. This at once simplifies the whole problem from the theoretical point of view, and although other evidence has been obtained which leads to the same conclusion, Nichols was the first to place the proof beyond all doubt.

In the second place, the existence of series of constant wave-number differences in both fluorescence and absorption bands proves that the two are similar in structural type. Then again, the proof of the observation of some of the component wave-numbers, both as absorption and emission lines, would strengthen the view that these frequencies are characteristic of the molecules, and that it is the condition in which the molecules exist that determines whether these lines appear in emission or absorption.

There can be no question that Nichols' work has very materially contributed to our knowledge of fluorescence emission.

Tesla Luminescence Spectra.—All the phenomena of fluorescence so far described have been those excited by light. A very important advance in the technique of the excitation of luminescence has recently been made by McVicker, Marsh and Stewart,[1] who have succeeded in rendering the vapours of certain organic compounds luminescent by means of the Tesla discharge. In their first paper these authors describe the Tesla luminescence spectrum of benzene, and as their results are of considerable interest these may be described in some detail. The experimental arrangement is very simple, and is shown in Fig. 82. The cell in which the vapour is excited is a glass tube

[1] *Trans. Chem. Soc.*, **123**, 642 (1923).

about 1·75 inches in diameter, closed at one end by a quartz window. At the other end is fitted a stopper, through which there passes a mercury electrode enclosed in a glass tube. The two side tubes, 11 and 12, serve as inlet and outlet for the vapour under examination. The exterior of the glass tube is wrapped round with foil, which forms the second electrode. Round the whole cell is placed a double-walled steel jacket, provided with three side tubes. Through one of these tubes is introduced a thermometer, whilst the other two may serve as inlet and outlet for the vapour of a liquid with constant boiling-point. In actual practice it is more convenient to fill the jacket with mercury and to heat it directly.

The high frequency apparatus employed contains 330 coils in its

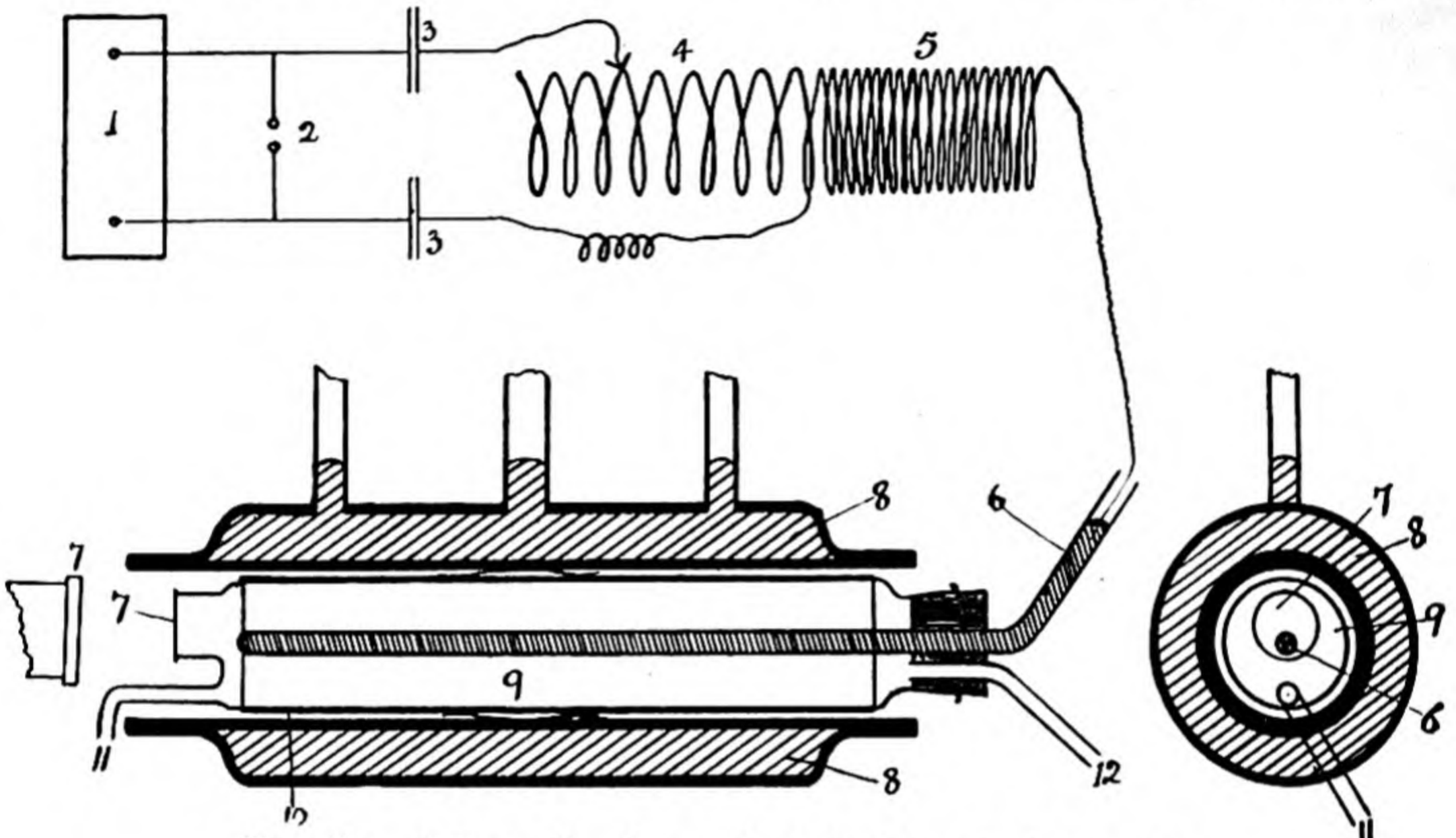


FIG. 82. (From the *Journal of the Chemical Society*.)

1. Induction coil.
2. Spark gap.
3. Leyden jars.
4. Primary of Tesla transformer.
5. Secondary of Tesla transformer.
6. Mercury electrode.
7. Quartz window.
8. Temperature jacket.
9. Cell.
10. Metal foil electrode.
11. Vapour exit tube.
12. Vapour inlet tube.

secondary (22 cm. in diameter), whilst its primary circuit is variable up to 30 coils. It is air-insulated, and the secondary is directly coupled to the variable primary. Since one end of the instrument is permanently earthed, it is sufficient to connect the end of the high tension secondary with the internal electrode of the cell and to earth either the steel jacket or the metal foil coating of the cell. Under these conditions a very steady Tesla discharge passes, as in an ozoniser, across the vapour contained in the cell. The Tesla transformer has four Leyden jars (capacity about 10 litres each) connected in pairs on either side of the zinc spark gap. As the source of current an 18-inch spark coil is employed.

When benzene vapour at ordinary pressures and at its boiling-point

is introduced into the cell, a green luminescence is observed, which shows only a fragmentary carbon spectrum together with some metallic and air lines. On reducing the pressure to 65 mm., benzene vapour at ordinary temperature emits a luminescence, the spectrum of which can readily be photographed. The spectrum consists of a number of fine bands which fall into seven groups, of which the seventh is represented by only one member, namely, the band at $1/\lambda = 3765$. Then follows a group of four strong bands with a narrow band accompanying each, and then two less strong and broader bands in which a primary and a secondary band may have been fused together. This arrangement is repeated in five more groups, with the difference that the secondary bands become too weak to measure towards the more refrangible end of the spectrum. The wave-numbers of these bands are given in Table LIX.

TABLE LIX.

Primary bands.	Group G.	Group F.	Group E.	Group D.	Group C.	Group B.	Group A.
1	—	3752	3652	3554	3454	3357	3257
	—	41	42	42	45	—	—
2	—	3736	3636	3537	3438	3339	3242
	—	25	25	28	28	—	—
3	—	3717	3618	3521	3422	3322	3229
	—	08	11	12	11	—	—
4	—	3703	3602	3504	3405	3308	3211
	—	93	92	98	—	—	—
5	—	3686	3586	3488	3390	3294	3194
	—	76	—	—	—	—	—
6	3765	3666	3570	3471	3376	3279	—

The wave-numbers of all these bands seem to be expressed by the general formula

$$1/\lambda = 98{\cdot}712n - 98{\cdot}712m/6$$

where $n = 33, 34, 35, 36, 37$, or 38, and $m = 0, 1, 2, 3, \ldots$ Of the above groups of bands, D and E are the strongest, F is not so strong, and the bands of A and B are broader and weak. In a later paper [1] the results are given of observations of the Tesla luminescence spectrum of benzene at a pressure of 1·6 mm. which revealed the existence of two new groups of bands, G and H, of smaller wave-length. These two new series do not seem to conform to the same type as do those recorded above. They are not so sharp and the intensity does not fall off so regularly from the head as in the other groups. Moreover,

[1] McVicker and Marsh, *Trans. Chem. Soc.*, **123**, 817 (1923).

the interval between the wave-numbers of the heads is about 92, instead of 98·712.

A very interesting fact in connection with the bands of this Tesla luminescence spectrum is that many of them are in the same positions as the component bands of the well-known absorption band group of benzene vapour. It is evident, therefore, that under the stimulus of the Tesla discharge benzene emits the same radiations as it absorbs when exposed to ultra-violet light. In view of the fact that the measurements of the wave-lengths of the Tesla bands do not lay claim to very great accuracy, it will be sufficient, with our authors, to compare these with the absorption measurements made by Hartley,[1] and this is done in Table LX.

TABLE LX.

Absorption.	Emission.	Absorption.	Emission.
3761	3765	3683	3686
3754	?	—	3676
3749-52	3752	—	3666
3738	3741	3656	?
3734	3736	3650	3652
3722	3725	—	3642
3716	3717	—	3636
3708	3708	3621	3625
3700	3703	3617-18	3618
3691	3693	—	—

It will be noted that, in general, the measurements of the Tesla luminescence bands are about two units larger than those of Hartley, but there is no question of the identity of the two sets of bands. The agreement is still better shown when the wave-numbers of the G and H groups of Tesla bands are compared with the absorption measurements made by Henri [2] as set forth in Table LXI.

It will be noted that the Tesla luminescence spectrum extends much beyond the ultra-violet absorption band group towards the longer wave-lengths, and, indeed, it covers the region of the fluorescence spectrum of benzene. This last spectrum is emitted by benzene when it is excited by the light rays lying within the absorption band, and was first discovered by Stark,[3] who examined alcoholic solutions of benzene. This spectrum was further investigated by Dickson [4] and Henri,[5] who gave more accurate measurements of the heads of the fluorescence bands as emitted by a solution. For the purpose of accurate comparison with the Tesla luminescence bands these results are of little use, since it is well known that the effect of the solvent is to shift the position of the bands by from 10 to 20 A. Assuming that

[1] *Phil. Trans.*, A, **208**, 384 (1908).
[2] *J. Phys. Radium*, **3**, 181 (1922).
[3] *Phys. Zeitsch.*, **8**, 81 (1907).
[4] *Zeitsch. wiss. Phot.*, **10**, 166 (1912).
[5] *Journ. de Phys. et le Radium* (6), **3**, 181 (1922).

TABLE LXI.

Band.	Absorption.	Emission.
H	3933·7	3935
	3917·5	3917
	—	3852-63*
G	3841·5	3843
	3834·7	3833
	3825·4	3827
	3818·2	3816
	3808·9	3810
	—	3894-01*
	—	3779-85*
	—	3764
	—	3756
	3749·4	3749

The bands marked with an asterisk are broad and indistinct.

the solvent shift is 19 units in the wave-numbers, McVicker, Marsh and Stewart were able to show that four of the fluorescence bands as measured by Dickson agreed very well with four of the bands of the Tesla spectrum of benzene.

In order to determine whether this coincidence is real, McVicker and Marsh undertook the observation of the fluorescence spectrum of benzene vapour which had not been previously recorded, and they succeeded in resolving it into 38 bands. The experimental method employed was described above on p. 254.

The measurements of the bands of the fluorescence spectrum of benzene coincide with those of the Tesla luminescence bands, and it is thus established that the Tesla discharge not only excites those vibrations which have hitherto only been recognised as absorption bands, but also those which characterise the fluorescence spectrum. In short, the complete analysis of the Tesla luminescence spectrum shows that it in reality consists of two parts which are single entities in so far as one is characteristic of the absorption spectrum and the other of the normal fluorescence spectrum.

The wave-lengths and wave-numbers of the fluorescence spectrum of benzene vapour are given in Table LXII., together with the Tesla luminescence bands in the same region.

McVicker and Marsh draw attention to the fact that the bands composing group F and indeed some of those of group E of the fluorescence spectrum coincide with bands in the absorption spectrum, a fact which can at once be recognised on comparing Tables LX. and LXII. In other words, the more refrangible end of the fluorescence spectrum overlaps the less refrangible end of the absorption spectrum and coincides with it in detail. An exactly similar phenomenon was observed by Nichols and his colleagues in the case of the uranyl salts and discussed fully above. This region was called the reversal region

TABLE LXII.

	Fluorescence.		Tesla.		Fluorescence.		Tesla.
	λ	1/λ			λ	1/λ	
Group G	2657	3764	3765	Group D	2815	3552	3554
					2825	3540	3542
Group F	2667	3750	3752		2828	3536	3537
	2674	3740	3741		2836	3526	3528
	2678	3734	3736		2841	3520	3521
	2685	3724	3725		2848	3511	3512
	2691	3716	3717		2855	3503	3504
	2697	3708	3708		—	—	3498
	2702	3701	3703		2867	3488	3488
	—	—	3793		2880	3472	3471
	2714	3684	3686				
	—	—	3676	Group C	2895	3454	3454
	2729	3664	3666		2903	3445	3445
					2909	3438	3438
Group E	2739	3651	3652		2917	3428	3428
	2747	3640	3642		2923	3421	3422
	2751	3635	3636		—	—	3411
	2757	3627	3625		2937	3405	3405
	2765	3617	3618		2950	3390	3390
	2770	3610	3611		2963	3375	3376
	2777	3601	3602				
	—	—	3592	Group B	2980	3356	3357
	2789	3586	3586		2995	3339	3339
	2802	3569	3570				

by Nichols, and there is no doubt that it is a perfectly general phenomenon. The overlapping of absorption and fluorescence has frequently been observed, and it has been claimed, somewhat unsoundly I think, that it constitutes a contradiction of Stokes' law of fluorescence, but the consideration of this must be postponed.

There is one detail in which the fluorescence and absorption spectra of benzene differ markedly from those of the uranyl salts. It has already been shown that the Tesla luminescence bands and the corresponding absorption bands (neglecting groups G and H) may be represented as a system of series with constant wave-number difference of 98·712. It may be seen from Table LXII. that the fluorescence bands may also be arranged as a system of series with a wave-number difference of 98-99. In the case of the uranyl salts the fluorescence band series have a constant wave-number interval of about 82, whereas the interval in the absorption band series is about 70, the two intervals being very different.

The fluorescence spectrum of benzene vapour has also been investigated by Pringsheim and Reimann,[1] who confine themselves, however, to purely qualitative observations. In place of the iron spark or arc as the source of the exciting radiation they made use of the mercury arc and the cadmium and zinc spark. They suggest that the fluor-

[1] *Zeitsch. für Phys.*, **29**, 115 (1924).

escence spectrum should be analogous in structure to the very complex absorption spectrum as revealed by the work of Henri,[1] but they confirm the results obtained by McVicker and Marsh with the addition of further bands of smaller wave-length. At pressures of 0·1 to 0·6 mm. the fluorescence spectrum consists only of a few weak bands which do not show any series relationships.

Phosphorescence.—The phenomena which next come under review differ markedly from those we have discussed in the foregoing. The essential difference, of course, consists in the fact that the emission continues or persists for an appreciable time after the excitation has ceased. This means that a state of excitation can exist which can be produced in a shorter time than it takes to return to the normal state. In the cases of simple fluorescence there are no rigid controlling conditions set by concentration, but in phosphorescence the influence of concentration and also of temperature is of very great importance. The problem in front of us is, therefore, more complex than that of pure fluorescence. The observations on record, too, are more diversified, since on the one hand we find the scientific investigation of the phenomenon, and on the other hand the utilisation of the phenomenon as a valuable adjunct in chemical work, such, for instance, as the separation of the rare earths from one another. Then, again, we have the excitation of phosphorescence by means of light and also by means of cathode rays and X-rays. It may, however, be stated that in the main the use of cathode rays, except in the excitation of rare earth phosphorescence, is restricted more to the spectacular than to the purely scientific side, this being due to the fact that it is not possible to define the wave-number limits of the energy absorbed by solid compounds when exposed to these rays. On the other hand, our problem is to some extent simplified by the fact that phosphorescence is entirely restricted to solid substances.

In view of the fact that the most valuable information has been obtained from a study of the phenomena of phosphorescence when excited by light, the exciting frequencies then being known, it is advisable first to describe this work, and subsequently to review its more general application. It is not possible within the limits set to this chapter to tell a story which in any way approaches a complete account of the work that has been done on phosphorescence, and it is incumbent on us to restrict ourselves to one or two of the outstanding investigations.

So far as the excitation has been caused by light, the technique of the production of the phosphorescence only requires very brief consideration. Since solids only are used, it is a simple matter to maintain a surface in front of the slit of a spectroscope or spectrograph and to stimulate the luminescence by directing a beam of light on to that surface by means of a lens. If desired, greater intensity of illumination of the slit can be secured by the use of a condensing

[1] *J. Phys. Radium*, **3**, 181 (1922).

lens. It is advisable, as far as possible, to restrict the exciting light to those rays which stimulate the phosphorescence so as to minimise the scattering of unwanted light rays when the substance is in the form of a powder. In the great majority of cases excitation is caused by ultra-violet light, and in order to screen off the visible rays a solution of *p*-nitrosodimethylaniline may be used, which was the case in some of Lenard and Klatt's experiments. As was previously indicated, the difficulty with solids is that there is no satisfactory method of measuring accurately the position of the absorption bands, especially in the case of powders. It is possible, by placing the substance in the focal plane of a spectrograph, the slit of which is illuminated by light rich in rays, to obtain information as to where the absorption band lies from the locus of the luminescence, but this is not very accurate.

As will be seen from what follows, the temperature and the concentration are of very great importance in phosphorescence. With regard to the latter, it will, of course, be understood that we are now dealing with solid solutions, and that in consequence it is necessary to make a number of preparations containing different amounts of the active principle in order to study the effect of concentration and the specific influence of the particular solvent or diluent used. Most important of all is the study of the persistence and the rate of decay of the intensity after the excitation has been stopped. The importance of the measurement lies in the fact that it is the rate of decay which is affected by temperature and concentration; in short, it is the fundamentally important characteristic of phosphorescence. In some cases where the persistence is long, that is to say the decay rate is slow, the measurements are simple enough in principle. A photometric method is used in which the intensity of the phosphorescence is matched against known standards of intensity having the same colour. In each individual observation a standard intensity is selected and the time interval, measured from the close of excitation, is noted which the phosphorescence intensity takes to decrease to that of the standard. By the use of many such standard intensities the complete rate of decay may be observed up to the stage when the phosphorescence intensity is too small to measure accurately. When the persistence is very short special apparatus is required which may now be described.

The Phosphoroscope.—In the measurement of the intensity of a phosphorescence band of short persistence and its decay with time it is necessary to use an apparatus which enables the phosphore to be viewed at definite and known intervals after excitation has ceased. Such an apparatus is known as a phosphoroscope, and several different forms have been used since E. Becquerel described the simple form used by him.[1] The fundamental principle of the instrument consists in the use of one, or possibly two, rotating sector discs, so adjusted

[1] *Ann. Chim. et Phys.*, **55**, 5 (1859); **62**, 1 (1861).

that the phosphore is invisible to the eye during excitation and becomes visible at a known interval after the excitation has ceased. The design employed by Wiedemann [1] may be briefly described. It consists essentially of three parts, the first of which is the driving mechanism constructed of a series of geared wheels operated by a weight and capable of rotating the sector at known and constant speeds. The second part is a short brass cylinder 83 mm. in internal diameter, closed at each end by a flat brass disc, the two discs being attached by screws. In each disc a round hole is drilled 11 mm. in diameter, with centres 30 mm. from the central axis, these two holes being exactly opposite to one another. Round the hole in one disc is attached a brass tube 20 mm. long, and with the same internal diameter as the hole, 11 mm. This tube carries a lens. In the rim of this short cylinder a rectangular opening 8 × 16 mm. is cut, its centre lying on the radius which passes through the centres of the round holes in the two end discs.

The third part of the apparatus consists of a single disc with a rim attached, the outside diameter of this rim being 80 mm. In the disc are cut four openings with centres 30 mm. from the central axis, these holes being equally distributed round the axis and having different shapes according to the particular type of observation required. In the rim four rectangular holes are cut 8 × 16 mm., these holes being symmetrically distributed round the axis, but out of step with the holes in the disc. The radius passing through the centre of each hole in the rim bisects the angle between the radii passing through the centres of the two adjacent holes in the disc. This disc and rim are mounted firmly on an axis inside the previously-described brass cylinder and rotated at a constant and known speed. The apparatus is so put together that the central disc of the rotating part is next to the outer disc which carries the tube and lens.

The method of observation is simple enough, and may be described as follows. The phosphore, on some suitable support, is introduced through the hole in the outer disc and so placed that it can be seen through the rectangular opening in the rim, and it is illuminated by a beam of light projected by the lens mounted in the tube attached to the disc at the opposite end. When the inner disc and rim are rotated light will only fall on to the phosphore during the times when the holes in this disc pass in front of the hole through which the beam of light passes. The phosphore is viewed through the rectangular hole in the rim of the brass cylinder and can only be seen when one of the holes in the rotating inner rim passes in front. Owing to the distribution of the four holes in the inner rim with respect to the four holes in the inner disc, the phosphore will be invisible during the time it is illuminated, but will become visible at a certain interval after the light has been cut off. The length of this interval depends on the speed of rotation of the inner disc and rim, and can be calculated if

[1] *Ann. der Phys.*, **34**, 446 (1888).

the speed is known. All that will be seen, therefore, is the intensity of the phosphorescence emission at a known interval after excitation, and this intensity will be a constant if the speed of rotation of the inner disc is a constant. The measurement of this intensity is made with a photometer. Wiedemann shows in his paper that the calculation of the rate of decay from a series of measurements made with varying speeds of rotation is not a simple one for more than one reason. He deduces a formula which he made use of in his work, and which need only be briefly referred to here.

Amongst this type of instrument mention may also be made of one designed and used by Nichols, it is characterised by its simplicity and adaptability to the study of phosphorescence of very small per-

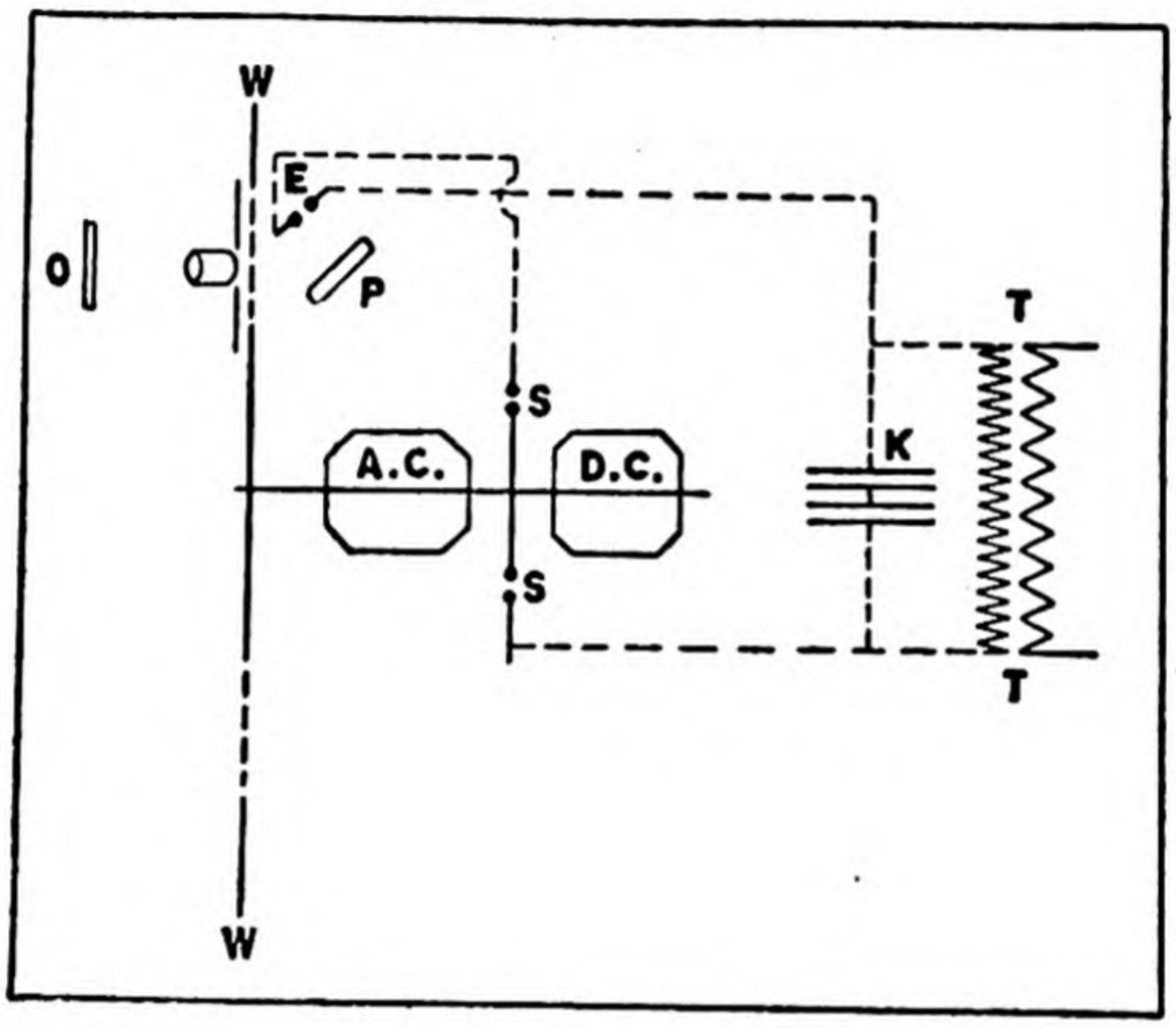


FIG. 83.

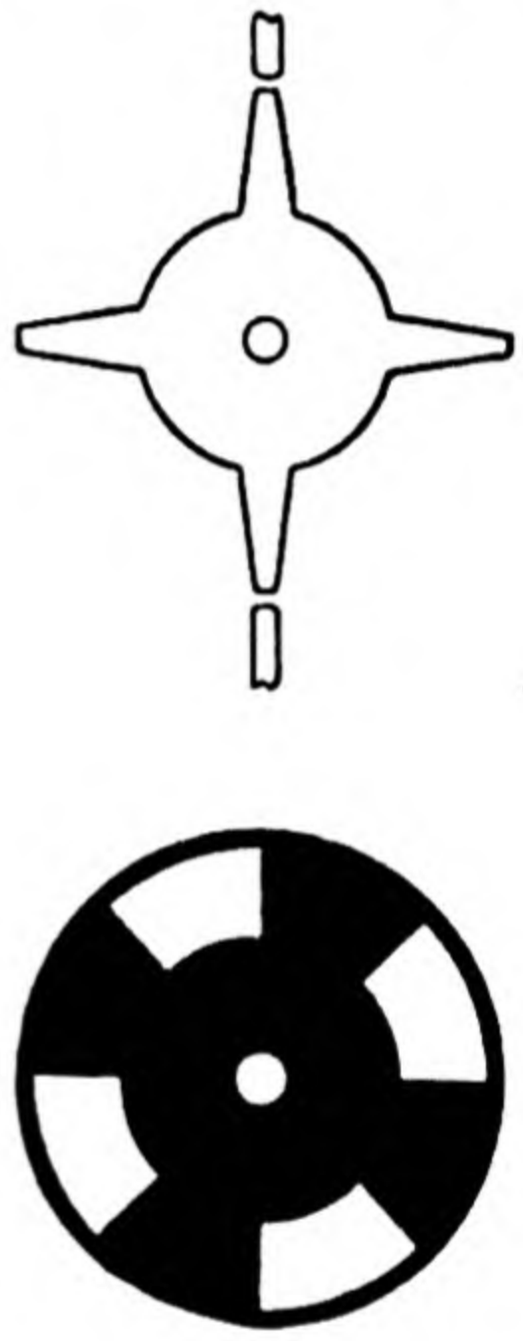


FIG. 84.

sistence. This instrument consists of a small synchronous alternating current motor A.C. (Fig. 83), and a small direct current motor with a common shaft. To one end of this shaft is attached a sector wheel WW, with four equal open sectors and four closed sectors, as shown in the lower portion of Fig. 84 corresponding to the four poles of the motor A.C. On the circuit of 60 cycles this motor, when brought to speed by the D.C. motor and then released, runs steadily at 30 revolutions per second. A step-up transformer TT, in the same alternating circuit, produces discharges at the spark gap or series of spark gaps E at each alternation, *i.e.* 120 times a second. Each discharge may be reduced to a single spark at the peak of the wave by means of the four-pointed star-wheel SS (Fig. 83), which is mounted on the shaft and carefully adjusted as to phase.

When the sector wheel is so adjusted on the shaft that the closed sectors conceal the phosphore during excitation by the spark, the

observer, looking through the apertures as they pass, sees the phosphorescence emission a few ten-thousandths of a second after the spark has passed. By shifting the sector wheel on the shaft, it is possible, without variation of the speed of rotation, to make observations at the very beginning of the phosphorescence and to compare by simultaneous vision the appearances just before and immediately after excitation, or the earlier and later stages, up to about 0·004 second.

We are now in a position to consider the results that have been obtained in the study of phosphorescence phenomena as excited by light. First and foremost in this field stands the research carried out by Lenard and Klatt, who were able, as the result of an exhaustive investigation, to reach conclusions which have proved to be of fundamental importance. It is true that they dealt with a particular type of phosphorescent preparation made by blending an alkaline earth sulphide with an active principle in the presence of a flux, but the results obtained with other substances have shown that their conclusions are of general application. Their work has proved a source of inspiration to many workers in this field and little or no excuse is needed for assigning it the premier place.

Lenard and Klatt's Work.—These authors investigated in the fullest detail the phosphorescence phenomena exhibited by the sulphides of the alkaline earth metals, when these contain small quantities of metallic salts as "impurities." In their early work[1] they satisfied themselves that a pure specimen of alkaline earth sulphide does not phosphoresce, and that in order to secure this phenomenon a mixture must be used which contains three essential components, namely, (1) the alkaline earth sulphide, (2) an active metal, and (3) an easily fusible salt. The last does not phosphoresce when blended alone with the sulphide. The metals employed in the form of their oxides were copper, bismuth, and manganese, and it was found that the colour of the phosphorescence depended on the particular sulphide and the active metal. The emission bands of copper, for example, lay in the blue-green with calcium sulphide, in the yellow-green with strontium sulphide, and in the red with barium sulphide.

Extraordinarily small quantities of the active metal are effective in producing phosphorescence. It was proved by Klatt and Lenard that at first the intensity of the luminescence increases up to a maximum as the quantity of the metal present is increased. Further increases in the quantity decrease the intensity to zero. The quantities which give the maximum effect are very small.

Lastly, it was proved that phosphorescent activity can only be secured by heating to redness. All attempts to prepare active mixtures at ordinary temperatures or in the wet way failed. During the course of this preliminary work it was found that pressure has a remarkable effect in destroying the activity of the preparations, a

[1] V. Klatt and P. Lenard, *Ann. der Phys.*, **38**, 90 (1889).

phenomenon which was dealt with in a separate paper.[1] When an active phosphore, as the preparation is called, is subjected to pressure in a mortar by means of a pestle the power of phosphorescence is destroyed. This can readily be detected by observing the phosphore in a dark room after excitation when the regions where the pressure has been applied appear dark and non-luminescent. Apart from its interest this phenomenon frequently introduces a difficulty in the preparation of the phosphores. If the material, after cooling, is not friable and requires to be disintegrated by friction, the phosphorescent activity is materially decreased. It is true that the activity can be almost completely restored by heat treatment at the same temperature as used in the original preparation, but it is obvious that the ready disintegration of the phosphore is to be aimed at.

A second effect which is produced by the application of pressure is the coloration of the phosphore. This coloration can easily be recognised, since, in general, these sulphide phosphores are white. It is of some interest, too, that the colour produced is only dependent on the particular alkaline earth sulphide used in the preparation. The same colour is always produced with a given sulphide whatever be the active metal present or the flux, and in consequence of this Lenard and Klatt attribute it to some physical modification in the sulphide.

Then, again, the effect of pressure is connected with a luminescence which is always emitted when an active phosphore is submitted to pressure. The phenomenon is not restricted to these phosphores, since it may be observed with other active substances. The platinocyanides, for instance, are sensitive to pressure, the crystalline barium salt becoming brick-red with a shade similar to that of the anhydrous salt. At the same time the phosphorescence changes from bright green to the dark red which is characteristic of the anhydrous salt. Similar changes are observed with the double platinocyanide of lithium and rubidium.

These preliminary results were confirmed and extended in a very exhaustive investigation carried out by the same authors.[2] As many as 800 preparations were made, and their phosphorescence studied, and the following general conclusions may be indicated before any details of these later results are discussed. In the first place, the original conclusion was confirmed that a pure substance does not phosphoresce, this phenomenon being essentially a property of a mixture in which the active constituent is present in very small amounts. In the second place, each active metal does not give only one, but a whole series of separate and distinct maxima of phosphorescence or emission bands. The nature of the flux used has an influence on the visible colour of the phosphorescence, and this is due to the fact that different fluxes establish differences in the relative intensities of the emission bands of the active metal.

[1] P. Lenard and V. Klatt, *Ann. der Phys.*, **12**, 439 (1903).
[2] *Ibid.*, **15**, 225, 425, 633 (1904).

Then, again, it was found that in addition to copper, bismuth, and manganese, the following metals can be used in the preparation of phosphores: silver, zinc, lead, antimony, and nickel. The same statement as to the emission bands applies to these metals as to those of the first-named three metals, and the general conclusion may be given that the wave-lengths of these bands vary very little or not at all, all the observed changes being restricted to their relative intensities.

One of the first matters which concerns us is the method of preparation of the phosphores, and this may now be described, it being understood that each substance used has the highest degree of purity possible. In order to simplify the nomenclature, an abbreviated method of writing is rendered possible by the fact that the dominating influence is always the metal. Thus, the symbol CaBiNa stands for a calcium sulphide phosphore containing bismuth as the active metal, and prepared with a sodium salt as flux.

In the first place, we may consider the preparation of the sulphides of the three metals, calcium, strontium, and barium. In the case of calcium the oxide is heated with sulphur when the following reaction takes place

$$4CaO + 4S = 3CaS + CaSO_4.$$

The stoichometric proportions of the reagents are 2 grams of the oxide and 1·143 grams of sulphur, but some sulphur is always lost by volatilisation and an excess must be used, a maximum yield of sulphide being obtained with 2 grams CaO and 1·35 grams of sulphur. All the heating operations are carried out in a porcelain crucible lined with platinum foil. The resulting friable mass is used and referred to in what follows as the sulphide, since the presence of the sulphate is of no consequence. This last point was proved by using a sulphide prepared as above, and also a sulphide made by heating calcium sulphite which gives a mixture of sulphide and sulphate according to the equation

$$4CaSO_3 = CaS + 3CaSO_4.$$

Two phosphores prepared from these two sulphides showed no difference in the intensity or the colour of the luminescence, in spite of the greater relative amount of sulphate in the second. Although it would appear from this that the sulphide might be entirely replaced by sulphate, this is not the case, since preparations made with pure calcium sulphate in the absence of sulphide do not show any phosphorescence after illumination by sunlight.

It must be remembered that, owing to the extraordinary small quantities of active substance which are sufficient to produce a measurable amount of phosphorescence, when the calcium sulphide is mixed with the various fluxes and heated, the product nearly always shows some luminescence which, as a matter of fact, is due to minute traces of copper. In the final preparations of the phosphores containing

other active metals this copper phosphorescence is in no way evident, and thus it may be concluded that when an active metal is present in exceedingly small amount the phosphorescence of a second metal present in greater amount can mask that of the first.

In the preparation of the phosphores the active metal is added in the form of its nitrate in solution, except in the case of antimony, when the tartrate is used. Solutions of known concentration are used and a measured quantity is employed in each case. Weighed quantities of the sulphide and flux are mixed together and then spread out over the bottom of the dish, a small cavity is made in the surface by means of the pestle, and the cavity is filled with ten to fifteen drops of absolute alcohol, the necessary number of drops of the metallic salt solution being added last. The whole is gently ground up together so as to secure equal distribution of the metallic sulphide throughout the whole. The mixture is then placed in a platinum lined porcelain crucible and heated at a bright red heat in a Hempel oven, usually for twelve to twenty minutes. The importance of the type of heat treatment will be dealt with below.

The following may be given as typical calcium preparations :—

CaCuNa.	3 grm. Sulphide, 0·2 grm. Na_2SO_4, 0·77 grm. NaF, 0·002 grm. Cu.
CaCuLi.	3 grm. Sulphide, 0·2 grm. Li_2SO_4, 0·07 grm. CaF_2, 0·002 grm. Cu.
CaCuK.	2 grm. Sulphide, 0·15 grm. K_2SO_4, 0·0013 grm. Cu.
CaPbK.	2 grm. Sulphide, 0·12 grm. K_2SO_4, 0·1 grm. CaF_2, 0·0017 grm. Pb.
CaPbNa.	3 grm. Sulphide, 0·15 grm. Na_2SO_4, 0·08 grm. NaF, 0·00084 grm. Pb.
CaMnNa.	2 grm. Sulphide, 0·1 grm. Na_2SO_4, 0·05 grm. CaF_2, 0·00093 grm. Mn.
CaNiF.	4 grm. Sulphide, 0·3 CaF_2, 0·00006 grm. Ni, heated for 10 minutes, then ground up with more sulphur and again heated for 30 minutes at the highest temperature of the Hempel oven.
CaBiNa.	2 grm. Sulphide, 0·1 grm. Na_2SO_4, 0·05 grm. $Na_2B_4O_7$, 0·05 grm. CaF_2, 0·00048 grm. Bi.
CaSbNa.	3 grm. Sulphide, 0·15 grm. Na_2SO_4, 0·06 grm. NaF, 0·0013 grm. Sb.

In the case of strontium phosphores the sulphide is prepared by moderately heating an intimate mixture of 5 grams $SrCO_3$ and 2 grams of powdered crystalline sulphur. Mixtures of this sulphide with the various fluxes after heating show evidences of copper phosphorescence, but, as in the case of calcium, this is masked in the phosphores prepared from it. The following phosphores may be mentioned, the quantities being expressed in grams :—

SrCuNa.	4 Sulphide, 0·1 Na_2SO_4, 0·1 $Na_2B_4O_7$, 0·00018 Cu.
SrPbLi.	2 Sulphide, 0·3 Li_3PO_4, 0·02 CaF_2, 0·00014 Pb.
SrAgNa.	2 Sulphide, 0·06 Na_2SO_4, 0·00016 Ag, not too strongly heated.
SrZnF.	3 Sulphide, 0·1 CaF_2, 0·0005 Zn, moderately heated for 3 to 4 minutes, then ground up with some sulphur and heated moderately strongly for 12 minutes.
SrMnNa.	3 Sulphide, 0·1 Na_2SO_4, 0·00005 Mn.
SrBiNa.	3 Sulphide, 0·1 Na_2SO_4, 0·00024 Bi.

The preparation of barium sulphide is complicated by the tendency to form polysulphides which colour the product yellow and depreciate the phosphorescence. These may, it is true, be destroyed by prolonged heating, but this is unsatisfactory. If 10 grams $BaCO_3$ are

heated with 2·25 grams of sulphur, the maximum yield of sulphide is obtained, and the colour is practically white, but a longer period of heating is necessary than in the cases of calcium and strontium. The presence of copper is again indicated by its phosphorescence, but, as before, this has no deleterious effect. As typical phosphores, the following may be given :—

BaCuNa. 3 Sulphide, 0·03 NaF, 0·00024 Cu.
BaPbNa. 3 Sulphide, 0·1 Na_2SO_4, 0·00028 Pb.
BaBiK. 3 Sulphide, 0·1 $K_2B_6O_{10}$, 0·00024 Bi.

Brief reference was made above to the effect of varying the temperature and time of the heat treatment. In general, these have the greatest influence on the total intensity of the phosphorescence, that is to say, all the bands of each metal are equally influenced. To obtain the best results, that is the fullest development of the emission bands, it is advisable to heat the mixtures at a sufficiently high temperature and for sufficiently long, so that the binding effect of the flux can be exerted to its fullest extent and thus prevent as much as possible the oxidation of the sulphides. In some cases the relative intensities of the emission bands of a metal are affected to a remarkable extent by changes in the heat treatment. This is well exemplified by SrAgNa and SrAgLi phosphores, which with a slow heat treatment give a reddish phosphorescence, whilst with longer and stronger heating the colour becomes more and more violet. This is due to a relative increase in the intensity of the violet band caused by the increased time and temperature, the nature of the flux being of far less importance.

We may now turn to the results obtained by Lenard and Klatt in their investigation of the many phosphores prepared by them. In the first place, the effect of varying the flux may be mentioned, and the following general conclusions may be given. In the case of some active metals, such as zinc, bismuth and manganese, the nature of the flux has little effect on the colour of the phosphorescence, that is to say, the relative intensities of the bands of each metal are not influenced by the flux. On the other hand, with some active metals such as copper and lead, the colour of the phosphorescence is very materially affected by a change in the flux, it being possible by varying the flux to obtain two or more colours. Here it is found that salts which are chemically similar have the same effect, this being shown in two different ways. Amongst the salts of the oxygen containing acids, it is the metal which has the predominating influence. Thus all the sodium salts have the same influence, and so on. The opposite is true with the halides, since it is the halogen element which has the dominating influence, all the chlorides and all the fluorides having their own specific effects. These relationships are especially exhibited with the calcium sulphide phosphores ; in the strontium sulphide and barium sulphide phosphores the various fluxes fall into groups with similar effects, but in these cases the grouping is not so obviously based on chemical analogies.

The most interesting part of Lenard and Klatt's work is concerned with the spectroscopy of the phosphorescence exhibited by their phosphores. This investigation includes the characteristics of all the emission bands, their position and relative intensities and persistence, and the effects of temperature and selective excitation. The first section of this investigation deals with the general question of the individual bands given by each of the active metals at different temperatures, and their relative intensities and persistence. The luminescence was excited by sunlight and also by a beam of ultra-violet light obtained from a powerful carbon arc lamp and passed through a solution of *p*-nitrosodimethylaniline,[1] which transmits all wave-lengths between $\lambda = 3900$ and $\lambda = 2000$. By the use of a suitable phosphoroscope the persistence of the phosphorescence after the exciting rays had been cut off could be observed.

In order to understand the details of the investigation three phosphores may be instanced, after which the general conclusions may be given, it being impossible to quote the whole of the observations made with all the different phosphores. As one of the simplest cases we may take the case of CaNiF which, when excited by ultra-violet light at ordinary temperatures, exhibits a band in the red, CaNiFα, at $\lambda = 0{\cdot}64\mu$, and a faint luminescence in the green. When the phosphore is exposed to the complete spectrum given by a quartz spectrograph it is found that the green luminescence is due to a specific band in that region, CaNiFγ_1, which is not readily excited by the ultra-violet light through the filter. At — 180°, excitation by ultra-violet light gives a third and narrow band, CaNiFβ, in the yellow, the red α band not being visible. Lastly, at + 200°, blue-violet appears in the luminescence spectrum, this being due to a fourth band, CaNiFγ_2, in this region. As regards the persistence of these bands, the α band has a definite persistence, whilst the γ_1 band vanishes immediately the exciting light is cut off.

SrMnNa—This phosphore, on excitation by ultra-violet light, exhibits a bright luminescence, the spectrum of which extends from the red to the middle of the green. Observation of the spectrum, immediately after stopping the exciting light, shows that the red portion vanishes forthwith, and there soon only remains a rather narrow band with long persistence in the yellow-green. The rapidly vanishing red portion appears equally quickly on excitation, whilst the long persistent green band is slow in developing. When this phosphore has lost all its phosphorescence and is suddenly exposed to ultra-violet light, the luminescence in the first instant is red in colour, and then the colour changes slowly (in about two seconds) to green. When the phenomenon is spectroscopically examined it is seen that a red band, SrMnβ_1, first appears quite alone and its wave-length can be measured, $\lambda = 0{\cdot}6\mu$. Excitation by the complete spectrum shows that along with the slow appearing yellow-green

[1] Wood, *Phil. Mag.*, **5**, 257 (1903).

band, SrMnα, there is a third band in the green, which is more rapid in its appearance and may be designated by SrMnβ_2. The wave-length of the α band is 0·56μ, whilst that of the β_2 band is about 0·54μ.

The SrPb phosphores reveal a more complex state of affairs. Their phosphorescence spectra show two maxima separated by an interval. One of these maxima in the yellow-green, SrPbα, is very strongly developed with SrPbNa, and its wave-length can be measured. The values found with SrPbNa at — 45°, 17°, and 200°, and with SrPbLi at 17° agree well, the mean being $\lambda = 0{\cdot}55\mu$. The second maximum is very broad, and extends from the blue with increasing intensity into the violet; it is particularly well shown by SrPbK and SrPbLi. The broad band consists of three separate maxima, as can be seen from the following observations. In the first place, in the case of SrPbLi, where the violet portion is the most intense, this colour fades much more rapidly than the blue and indigo after extinction of the exciting light. Further, the violet portion entirely vanishes at — 180°, only the blue and indigo being seen. This must be due to a violet band, SrPbβ, and the wave-length was found with SrPbK and SrPbLi at — 45° to be 0·41μ. The remainder of the broad band, the blue and indigo portions, consists of two bands, since at — 180° with SrPbK a strong maximum is observed in the indigo region, SrPbβ_2, the blue being absent, and since with SrPbLi a weak maximum is observed in the blue, SrPbβ_1, the violet now being absent. The wave-lengths of the β_1 and β_2 bands are 0·47μ and 0·44μ respectively. The different effects of the various fluxes are well shown by this group (SrPb) of phosphores. The sodium salts give the α band only with considerable intensity, lithium salts give the β group, especially β_3, whilst potassium salts give the α group and the β group with medium intensity.

Lenard and Klatt arrived at the following general conclusions. The different colours of the phosphorescence, caused by the use of different fluxes, are due to the combined effect of the same definite absorption bands which characterise a particular metal disseminated through a particular alkaline earth sulphide. Each flux strengthens some of these bands compared with others which are weaker or absent. The flux not only affects the intensity of the band, but also its period of persistence. No shift in the position of the bands in the spectrum was ever observed.

The intensity and persistence of a band vary independently of one another, for if a certain flux increases the intensity it decreases the persistency and *vice versa*. Thus the BaCuα_2 band with Li_3PO_4 has a great intensity with small persistence, whilst with NaF the intensity is rather less and the persistence much greater. So far as can be stated without measurements being made of the intensities it would seem that no variations in the fading of the bands in the afterglow occur beyond those which can be expressed as differences in the period of persistence. All bands appear to fade according to the same law, but at different rates.

It is quite different, however, with the total emission power of the different phosphores, since each one has its own peculiarities. This can be seen at once from a comparison of three phosphores, SrCuNa, BaBiNa, SrZnF, all three of which luminesce with the same total intensity during irradiation by ultra-violet light and one-quarter of an hour after the irradiation is stopped luminesce with the same smaller intensity. The fall in the intensity from the initial value to the final value is different in each of these three cases. The luminescence of SrCuNa falls in the first tenth of a second to a small fraction of its initial value and then decays very slowly. The luminescence of BaBiNa at first decreases very much more rapidly than it does later, but the initial fall in intensity is much less than in the first case, and it extends over a period of several seconds. With SrZnF an initial fall of intensity is so little marked that it is difficult to detect any change in intensity when the irradiation is stopped. It may be shown that these three characteristic phenomena of the decay of the total luminescence is due to the individual bands of the active metal present, each of which has its own specific rate of decay.

It is very important that not one of the emission bands observed by Lenard and Klatt exhibits at first a slow rate of decay and afterwards a more rapid rate. This was first noted by E. Becquerel, who also concluded that the phenomena connected with the decay of the total luminescence are due to the summation of the effects due to different portions with different rates of decay. Becquerel did not use phosphores of known chemical constitution, but he was able to show by photometric measurements of intensity that the rate of decay can be expressed as the sum of several exponential functions of the time.[1] Lenard and Klatt point out that Becquerel dealt with phosphores containing several active metals, whereas they studied phosphores which were pure in the sense of there being only one active metal present.

As already stated, the rate of decay of every band is indissolubly bound up with its rate of excitation ; all bands with rapid decay are rapidly excited by all the methods of excitation, and all bands with long persistence are only slowly called into being. The complete excitation of bands of long persistence may take several minutes, but the time is inversely proportional to the intensity of the exciting radiation. In weak ultra-violet light, phosphores which give bands of long persistence reach their maximum intensity only slowly and sluggishly, *e.g.* CaBiNa, CaMnNa, SrZnF, SrBiNa, and SrAgLi. On the other hand, phosphores such as CaCuNa (β-group), SrCuNa, SrCuLi (α-band), which exhibit bands of vanishingly small persistence, reach almost full luminescence immediately. An interesting example of this is given by a phosphore, such as CuBiNa, which is characterised by bands of different persistence. If this phosphore is excited for a period of one second, it will behave as one which gives only a

[1] *La Lumière*, I., 285 (1867).

rapidly vanishing band. If, on the other hand, it is excited for a period of three minutes, the long persistence bands are fully excited, and the substance behaves as a body with a long persistent phosphorescence.

The second section of Lenard and Klatt's work deals with the influence of temperature, which is twofold: The first is the effect of different constant temperatures on the luminescence, and the second is the effect of raising the temperature in increasing the luminescence of a previously excited phosphore. Each of these may be dealt with separately, and first we may consider the luminescence phenomena as observed at different constant temperatures. These observations were simplified by the use of the ultra-violet filter, so that a more or less constant means of excitation was used. The mean temperatures employed were five in number, namely, — 180°, — 45°, + 17°, 200°, and 400°. The visible colour or colour-shade of the luminescence is changed by the temperature, but this is due to the summation of all the bands characteristic of the active metal present, each band being influenced in its own way by the temperature changes. The temperature influences the intensity and the persistence of a band, but never alters its position. The intensity and persistence of each band are changed independently, for an increase of temperature can increase the persistence and decrease the intensity or *vice versa*. Certain bands may be increased in persistence at a lower temperature without any material decrease in intensity. Again, the bands CaCuα and SrCuα have a high intensity, between — 180° and + 300°, but a notable persistence is only observed between — 45° and + 17°.

The influence of temperature is independent of the particular flux used, that is to say, the specific influence of a given flux on the intensity and persistence of a particular band is the same at all temperatures, and so also is the influence of temperature on a particular band the same with all fluxes.

It is true in general of all emission bands that there is an upper temperature limit above which no excitation by light can take place. This limit is different for different bands: with some bands the limit lies near red heat, with many the limit lies much lower. The lowest temperature limits at which luminescence suddenly ceases are shown by the barium sulphide phosphores, and in particular BaPb and BaBi, the temperature limits of which lie near 100°. A lower temperature limit was not found by Lenard and Klatt, nor was any indication found of the existence of such. The lowest temperature employed, — 180°, differed in no way in its influence on the activity of their phosphores from any other temperature below the upper limit.

Between — 180° and the upper temperature limit new bands may appear and exhibit considerable intensity, whilst the older ones observed at room temperature disappear. Such new bands are CaNiβ and CaMnβ, which appear below — 70°, and CaNiγ_2 and CaSbβ, which appear at high temperatures a little below the upper limit of all luminescence. Striking examples of complex changes in the bands caused

by temperature change are shown by CaBi and SrBi, whilst great stability under temperature changes is shown by CaCu, CaPb, SrCu, and SrPb phosphores, with the result that their emission spectra remain constant over the whole temperature range. It is noteworthy that some bands, *e.g.* CaCuγ and CaPbγ, have two maxima, one at low temperatures and the other at high temperatures. This is undoubtedly due to the presence of two closely situated overlapping bands.

A characteristic opposing influence is sometimes caused by temperature change on the different bands of the same phosphore, if a new band appears as the result of the temperature change. The most striking instance of this is afforded by CaNiF, which at — 180° exhibits the β-band alone with good persistence. When the temperature is raised to about — 70°, the red α band makes its appearance and the β band is weakened, the two having about half their maximum intensity. At this point the persistence of each band is vanishingly small. On raising the temperature to + 17° the α band alone is visible, and it now has a definite persistence.

In general, the emission bands become narrower and more sharply defined at low temperatures, and as a result closely situated bands tend to be better resolved. At high temperatures the bands broaden and run into one another to form a continuous spectrum. With phosphores having low upper temperature limits this fusion of separate bands is pronounced at room temperature. When many bands fuse together in this way the result is frequently seen of a white luminescence.

The second influence of temperature is the increase in intensity of phosphorescence emission caused by heating an active phosphore. The general observation that a rise in temperature increases the intensity of emission by an excited phosphore and that fall in temperature decreases it has long been known, having first been discovered by E. Becquerel with fluorspar. The phenomena were studied in detail by Lenard and Klatt with their own phosphores, and their results are of considerable importance. Without previous excitation a phosphore will not luminesce on heating. If the luminescence of an excited phosphore has been caused to vanish either by long keeping in the dark or by heating above the upper temperature limit, then the substance cannot be induced to luminesce by heating or by cooling and subsequent heating. It is evident, therefore, that the emission on heating is due to the release of the previously excited phosphorescence. This release can be carried out if desired in stages, when each successive heating releases only that amount of phosphorescence left over after the previous emission. As an example of this BaPbNa may be taken. This substance, after irradiation at — 180° with sunlight, phosphoresces brilliantly when heated gently over a small, non-luminous flame. If the temperature is raised to 200°, the emission soon ceases, and if the substance be then cooled to — 180° and then once again heated, no trace of further luminescence can be detected. If, however, .during the first period of heating the sub-

stance is plunged into liquid air before the radiation has ceased, then on again heating it the radiation appears once more, with an intensity about equal to that which was quenched by the cooling. The same phenomena can be seen with phosphorescent zinc sulphide.

Fluorspar, on the other hand, behaves rather differently. If this material is activated by long exposure to sunlight and then brought to 90°, a strong visible luminescence appears which persists for several minutes. When this emission has ceased, the crystals are cooled for five minutes and then once again heated to 90°. There then appears the same visible luminescence with the same persistence. This sequence may be repeated several times with the same result, except that the luminescence has a smaller intensity at each repetition. This phenomenon appears at first sight to be a direct contradiction of the previous statement, but the probable explanation is a simple one, it being remembered that the upper temperature limit of luminescence is much higher than 90°. The complete phosphorescence spectrum of fluorspar contains many bands, some in the visible and some in the ultra-violet, and the persistence of the former is much smaller than that of the latter. Consequently, when the visible radiation at 90° ceases the ultra-violet radiation still continues, and Lenard and Klatt suggest that when the fluorspar is cooled activation of the latent visible phosphorescence is caused by the ultra-violet radiation. The contradiction would, therefore, be only an apparent one. It must, of course, be understood that when heated to the upper temperature limit, the whole of the phosphorescence, visible and ultra-violet, is radiated and cannot be restored by cooling and subsequent heating.

The spectrum of the light emitted during the rise of temperature is the same as that of the after-glow at constant temperature, and at every instant it is the same as that of the after-glow at that temperature. There appear, therefore, with strong intensity those bands which have long persistence, with weak intensity those bands which have smaller persistence, whilst the bands with vanishingly small persistence do not appear at all. The phenomena of luminescence due to heating are thus the opposite of those observed at constant temperature.

It follows from the foregoing that the luminescence obtained on heating an activated phosphore is not due to a special kind of excitation. It is due to the release at a special temperature of the excitation stored up in the phosphore during the previous irradiation; in other words, the phenomenon is due to the radiation of energy which the phosphore absorbed and stored up during its exposure to light.

These results agree in general with the view held by E. Becquerel, namely, that each phosphore has the power of storing energy in readiness for phosphorescence, and that this power is less at high temperatures than at low temperatures. This view, as will be shown below, requires extending, since each band must be considered separately,

and, further, each band is characterised by three temperature conditions.

In the third section of their investigation Lenard and Klatt dealt with the relation between the wave-length of the exciting light and the intensity of the phosphorescence, and in so doing considered every band separately. Once again we may confine ourselves to the conclusions which they drew from their observations. Every phosphorescence band has its own region of exciting wave-lengths, and in the visible and ultra-violet regions there is, in general, more than one maximum at which excitation of each band can occur. The excitation region rarely extends far into the visible region of the spectrum, and if visible rays can excite phosphorescence, then it follows from the principle of the storage of energy that such excitation may establish a visible colour in the *activated* phosphore. Such colorations are clearly evidenced in many cases, but in a few no visible coloration seems to be produced. The suggestion is made that in the latter exceptional case absorption takes the place of light of other wave-lengths as well as the exciting light. It was further found that in none of the sixty-four bands which were accurately investigated was Stokes' rule disobeyed.

The persistence of a band is independent of its method of excitation, whether this be effected by light or by cathode rays. Bands, which with a given flux and at a given temperature have vanishingly small persistence, remain so under all kinds of excitation, the same being true of bands with finite persistence. Poor excitation only decreases the intensity and does not hinder the persistent after-glow. Some persistent bands, if not all of them, need much greater light intensity to excite them to their fullest extent than do the bands with no persistence.

The exciting wave-lengths are independent of the flux and the temperature; they are unalterable characteristics of the bands. A phosphore absorbs and stores up the energy for each band, and this energy cannot be utilised for the excitation of any other band characteristic of that phosphore. In the case of bands of no persistence, or instantaneous bands, which at higher temperatures develop a finite persistence, the storage of the exciting energy is remarkably complete and the activated phosphore can remain unchanged for a long time until, on heating to the higher temperature at which the bands are persistent, the energy escapes and the bands become visible. In the case of instantaneous bands which do not become persistent at higher temperatures the energy necessary for their excitation cannot be stored up.

It would seem to follow from the foregoing that there must be three conditions of temperature which determine the persistence of a band, namely, a temperature region throughout which the band has a finite persistence, and a higher and a lower temperature region throughout both of which the band has vanishingly small persistence. These three conditions may be called the lower instantaneous state,

the persistent state, and the higher instantaneous state, the three being in ascending order of temperature. As a matter of fact, the experimental observations support this conception with the great majority of bands; in a few cases the observations are incomplete, and in no case do the observations contradict it.

After discussing some analogies between the behaviour of different bands, Lenard and Klatt conclude with some general conclusions based on their complete series of observations. The multiplicity of the phenomena which are to be observed with a single phosphore render it impossible to conceive of them being due to a single entity. A recognition of this is forced on us when it is proved that the phosphorescence emission consists of a number of individual bands, each one of which is characterised by its own properties. These properties have already been described, but a few words may be added with regard to the three band states, which are defined by the temperature, because these would seem to be of great importance in connection with any theory of phosphorescence, as will be shown later. In the first or lower instantaneous state two processes occur simultaneously in the excitation of a given band, namely, an instantaneous appearance and disappearance of the band (the latter being observed when the excitation ceases), and also a storing up of the energy which increases asymptotically with the persistence of the band in the after-glow and the intensity of the exciting light. As already stated, this storage of energy is extraordinarily stable, and the energy remains locked up until the temperature is raised sufficiently to bring the band into the second state, when the band begins to be visible and the stored up energy is radiated. Both these processes are carried out by light of the same wave-length and they take place independently of one another. The latter statement means that if the first process fails, the storage of energy takes place without the band being visible, and that if the second process fails the band is visible but no energy is stored. It may be pointed out in passing that Lenard and Klatt only consider the *visible* evolution of energy during the excitation process and the storage of the energy. Further, this alternative does not seem to agree with Lenard and Klatt's statement that they were unable to find any lower temperature limit to phosphorescence.

In the second or persistent state energy is stored up during the excitation, but the storage is not so complete as in the first state, since the band is visible when the excitation ceases. As in the first state, the storage increases asymptotically with the persistence of the band in the after-glow and the intensity of the exciting light. What is actually seen during the excitation is a steady increase in the intensity of the band to a constant maximum and, after the exciting light is removed, there is a steady decrease in the intensity as the stored up energy is radiated.

In the third or upper instantaneous state no storage of energy takes place, and when the excitation begins the band appears at once with full intensity, and when excitation ceases the band vanishes

at once. The upper limit of the range of temperature, within which this state exists, coincides with the upper temperature limit to all phosphorescence.

In concluding this account of Lenard and Klatt's work particular attention may be drawn to some of their results. In the first place, their observation of the effect of pressure on an activated phosphore may be referred to. They found that the effect of pressure is to destroy the power of phosphorescence emission possessed by the phosphore, this loss of power being associated with the appearance of luminescence. Not only do we find in this a typical case of what is known as triboluminescence,[1] but also a direct connection between triboluminescence and latent phosphorescent activity. It follows, therefore, that the energy which is stored up in the phosphore during activation can be released either by heating, when the phenomenon is known as thermoluminescence, or by mechanical disturbance, when we call it triboluminescence. There must be an intimate relation between the three manifestations, each of which is associated with a substance that has been converted into a metastable condition by the absorption of light energy. This relation at times seems to have been missed. In this connection reference may be made to a statement by Guntz [2] that phosphorescent zinc sulphide may be re-energised by immersion in liquid air, the first effect being the complete quenching of the phosphorescence emission. On allowing the sulphide again to become warm the emission reappears; he says that with phosphorescent calcium sulphide, however, no fresh absorption of energy takes place on cooling. It would surely seem that this interpretation is incorrect, and that the explanation has already been given by Lenard and Klatt. At low temperatures the rate of phosphorescence emission is very greatly decreased, and the energy then remains stored up in a latent state, only to appear again as phosphorescence when the temperature is raised.

A second observation made by Lenard and Klatt, which may be emphasised, is the power of a single active metal to give more than one phosphorescence emission band, each with its own activating set of frequencies. In the phosphores studied by them this existence of the molecules in differently responsive states seems to depend on the three factors, temperature, nature of solvent or diluent, and concentration. On the other hand, it has been shown possible to prepare pure compounds in two different states, which have different colours and therefore different absorption bands, and which exhibit different fluorescence emission. An instance of this is given by Levy,[3] who states that it is possible to prepare three different modifications of barium platinocyanide, $BaPt(CN)_4$, $4H_2O$, two of which are crystalline and the third is amorphous. All three are chemically identical,

[1] A valuable paper on triboluminescence phenomena was published by Imhof, *Phys. Zeitsch.*, **18**, 78 (1917).

[2] *Comptes Rendus*, **179**, 361 (1924).

[3] *J. Röntgen Soc.*, **12**, 13 (1916).

but display totally different physical properties, as shown in Table LXIII.

TABLE LXIII.

	Crystalline A.	Crystalline B.	Amorphous.
Colour . .	Orange.	Apple-green.	Brick-red.
Crystalline form	Identical.	Identical.	None.
Fluorescence .	Very feeble.	Very brilliant.	None.

The fluorescence of the green salt is fifty times as intense as that of the orange salt, and further, the specific gravity of the two crystalline modifications is different. When each of the crystalline modifications is powdered in a mortar it becomes brick-red in colour and loses its luminescence. This change has been attributed to loss of water, since the dihydrate, $BaPt(CN)_4$, $2H_2O$, is red and non-fluorescent, but Levy states that it is due to the conversion into the amorphous form, which can also be brought about by the prolonged action of X-rays. He further considers that the difference between the two crystalline salts is one of stereoisomerism.

A somewhat similar phenomenon is recorded by Schleede and Gruhl,[1] who prepared three different varieties of zinc silicate, $ZnSiO_3$, containing traces of manganese. These three varieties exhibited green, yellow, and red luminescence respectively, under the influence of X-rays. All three are modifications of the same substance, since the two which show yellow and red fluorescence change into the third variety at 900°. It was concluded that the difference in fluorescence activity was due to different crystalline structure, evidence for this having been found by means of the X-ray spectrometer.

One of the most important of Lenard and Klatt's observations is the cardinal importance of the solvent or diluent in phosphorescence emission, when the term is used to denote the persistence of emission after the excitation has ceased. A substance in the pure state may luminesce on exposure to light, and at the same time store up energy; the same also occurs with phosphores at temperatures which lie within the lowest of Lenard and Klatt's three temperature regions. On the other hand, no pure substance exhibits phosphorescence emission in the strict sense, this only being observed when the active principle is in solid solution in a diluent. This essential condition was stressed very strongly by Urbain and Bruninghaus, whose work will presently be considered. Even if Lenard and Klatt did not emphasise this condition in communicating their results, it is quite evident that they discovered it. They certainly pointed out the remarkable phosphorescence activity exhibited by minute traces of an impurity in an otherwise pure substance, and thereby found the explanation of the brilliant

[1] *Zeitsch. Electrochem.*, **29**, 411 (1923).

phosphorescence exhibited by many compounds which contain such small traces of impurities as to be beyond detection by the ordinary methods of chemical analysis.

The power of certain pure substances to absorb and store up radiant energy as latent phosphorescence is worthy of further consideration, more particularly in view of the fact that the metastable state thereby produced from a colourless compound very frequently is characterised by a visible colour. The production of an amethystine modification of silica glass by the action of ultra-violet light has already been referred to.[1] More interesting still are the highly coloured metastable states of the alkali metal chlorides, fluorite, etc., which can be obtained from the normal colourless varieties by the action of X-rays and cathode rays. It has been suggested that the blue form of sodium chloride, for example, is due to actual decomposition with formation of traces of metallic sodium.[2] This suggestion is negatived by the fact that a neutral solution is obtained when the coloured modification is dissolved in water. This has been proved by Brode.[3] Since these coloured modifications revert with radiation of energy to the colourless form on heating, it would seem that they conform in every way to the Lenard and Klatt phosphores in the lowest temperature region, that is to say, the coloured form is the metastable state produced when the normal colourless form stores up energy.

There is yet another fact which has been finally established, namely, that with a definite amount of excitation the persistence and intensity of an emission band are in inverse ratio to one another, that is to say, the longer the persistence the smaller the intensity, and *vice-versa*. This must be true if it be accepted, as Lenard and Klatt indeed assumed, that activation means the absorption of energy. After a definite quantity of energy has been absorbed, then in the radiation of that quantity in the form of phosphorescence emission the velocity must affect the persistence and intensity in opposite senses. Since the phosphorescence emission is the integration of the individual radiation by a number of molecules, it is clear that the intensity must decrease with time as the number of molecules in the activated state becomes smaller. This fall of intensity with time measured from the instant of quenching the excitation is known as the rate of decay, and reference has already been made to the measurement of this in the section dealing with the fluorescence of the uranyl salts. It is evident that the intensity will not be linearly proportional to the time, and it has been proved that in most cases a straight line is obtained when the time is plotted against the reciprocal of the square root of the relative intensity, that is to say, $I^{-\frac{1}{2}}$. In a few cases straight lines are obtained by varying the exponent of I.

[1] See p. 101.

[2] Goldstein suggested that it is due to a distension of the molecule without actual disruption. *Nature*, **94**, 494 (1914).

[3] *J. Phys. Chem.*, **30**, 507 (1926).

The general expression for the decay curve is

$$\frac{I}{I_0} = \frac{1}{(a + bt)^n}$$

where I_0 is the initial intensity, I the observed intensity at the time t, and a and b are constants. If I is expressed relatively to I_0 then

$$I^{-1/n} = a + bt.$$

In the majority of cases $n = 2$, that is to say, the relation between time and $I^{-\frac{1}{2}}$ is linear, but Becquerel found cases in which n has values which differ from 2. Ives and Luckiesh [1] found that in the case of zinc sulphide $n = 1{\cdot}03$.

It has been found, however, that the problem is not quite so simple, since the decay process consists in general of two stages. If the time is plotted against $I^{-\frac{1}{2}}$, the two stages are at once shown by two straight lines which have different slopes to the time axis, the second process being slower than the first. In order to explain these statements some results obtained by Nichols, Howes, and Wilber [2] may be described. These authors examined the luminescence given by several samples of calcite obtained from Franklin Furnace, N.J., under excitation by light and by cathode rays, and they also measured the rate of decay shown after each kind of excitation. In order to determine the law of decay of the cathodo-luminescence, a single crystal of the calcite was placed at the bottom of a V-shaped discharge tube and was viewed directly through the Lummer-Brodhun cube of the photometer. The comparison light for the reflecting zone was transmitted through a screen of ground glass or milk glass from a small tungsten lamp mounted on a long photometer bar. The approximate colour match was obtained by the use of a suitable orange-yellow colour screen.

The time of close of the excitation was automatically recorded on a chronograph, and the times when the intensity of the phosphorescence matched that of the comparison light placed at selected positions along the bar were indicated upon the same chronograph sheet by tapping a key in the chronograph circuit. The first observation was made as soon as possible, about 0·4 second, after the close of excitation, and they were continued for about 300 seconds.

When the results obtained with fresh calcite crystals were plotted time against $I^{-\frac{1}{2}}$, they were expressed by two straight lines at an angle to one another, the second line being less inclined to the time axis. This is clear evidence of two separate processes of decay, the second of which is slower than the first. The sudden change from the first to the second process took place at about 40 seconds after the close of excitation. It was found in the course of these measurements that at times the two processes merged into one another, with the result that two well defined straight lines were not obtained, but an

[1] *Astrophys. Journ.*, **34**, 173 (1911).

[2] *Phys. Rev.*, **12**, 351 (1918).

initial curve for the first period of about 50 seconds, followed by the normal straight line of the second process. This is also observed with the long persistence phosphorescence of substances other than calcite, and is always obtained when the material is subjected to simultaneous excitation of widely different intensities. It was further found that the same effect is obtained when the calcite has been exposed for a long time to the cathode rays and a coloured film has thereby been formed on the surface of the crystals.

As will be shown presently, the luminescence produced in calcite by photo-excitation is of very short duration, and entirely vanishes within 0·5 second. It is of interest, therefore, to examine the rate of decay of cathode phosphorescence during the first few tenths of a second, the earliest measurements just described being after a time interval of 0·4 second. For this purpose a special phosphoroscope was constructed which could be operated in a vacuum. The sector disc was driven by a shaft which passed through a specially designed stuffing box. With this apparatus it was found that in the initial period of 0·06 to 0·60 second there is an initial decay process which is faster than the two later processes. The decay rate during this first process is also represented by a straight line when the measurements are plotted in the usual way. Altogether, therefore, there exist in the case of the cathodo-phosphorescence of Franklin Furnace calcite three separate processes with decreasing rates of decay. It must be noted that the luminescence appears to be due to the presence of traces of manganese, and this is of importance, since some specimens of calcite do not show this phenomenon.[1]

The examination of the rate of decay of the photo-luminescence showed that it is, in the first place, extremely rapid, and, in the second place, of an entirely different type from that observed with the cathodo-phosphorescence. For this work a special type of phosphoroscope was also used, and the excitation was caused by the light from either the iron spark or the quartz mercury lamp. In general, the luminescence became vanishingly small at 0·5 second after excitation, and the time intervals of the measurements lay between 0·01 and 0·45 second. The results, when plotted in the usual way, revealed the existence of three separate processes, but with each successive process the rate increased instead of decreased, as is the case with cathodo-phosphorescence. This phenomenon is the same as that observed with the fluorescence of the uranyl salts, as previously described on p. 258.

So far as I am aware, no explanation has been found of the three successive processes in the decay of luminescence nor of the essential difference between the vanishing and persistent types. The only difference in the method of experiment is that in the one case excitation is caused by light and in the other by cathode rays. This difference, however, is real, since there is no question that the condition of cathode

[1] Stokes, *Phil. Trans.*, **142**, ii. 516 (1852); Sohncke, *Ann. der Phys.*, **58**, 425 (1896).

ray excitation corresponds to excitation at a smaller wave-length than the ultra-violet light. The problem is complicated by the fact that in certain cases the character of the individual processes is dependent on the temperature. Thus Ives and Luckiesh [1] found that the rate of decay of the phosphorescence of Lenard and Klatt's phosphore, BaBiK, is very different at 0°, 22°, and 35°. When time is plotted against $I^{-\frac{1}{2}}$ a curve is obtained concave to the time axis at 0°, at 22° the curve is linear, and at 35° it is markedly convex to the time axis. The last result seems to be only explicable by the existence of separate processes which are successively more rapid.

Then again, in all cases other than the uranyl salts the problem is still further complicated by the fact that the luminescence consists of more than one band. Nichols, Howes, and Wilber state that during the decay of the vanishing type the colour changes in the phosphorescence of substances, the spectra of which contain two or more bands differing in wave-length and persistence, are beautiful and most striking.

The question may well be asked whether the two bands are absolutely independent of one another. Is it not possible that the persistence of one band is modified by the other? It is true that the most natural view to take is that two bands are completely and absolutely independent manifestations, this being suggested by Lenard and Klatt's proof of their individuality. On the other hand, we have the remarkable instance of the self-activation of fluorite (see p. 303) which Lenard and Klatt themselves seek to explain by the utilisation for this special purpose of the latent energy. If this transference of energy can take place whereby, during radiation, the energy of the activated state giving one band can be increased at the expense of the activated state giving another band, then many of the difficulties which have arisen will disappear.[2]

In the last section of this chapter reasons will be given for the belief that fluorescence and phosphorescence are two different phenomena associated, respectively, with the activation and de-activation processes. I believe that even though fluorescence is associated with activation it will have a decay rate, which will be of a different type from that of phosphorescence, however rapid this may be. Unfortunately, this can only be an expression of opinion so long as we are without knowledge of the rate of growth of fluorescence after activation commences in those substances, the decay of which is of the vanishing type and has been measured. We know that the interval between the instant of excitation and the appearance of fluorescence is very short in some cases. Gottling [3] found that this interval with barium

[1] *Astrophys. Journ.*, **36**, 330 (1912).

[2] The suggestion of self-activation or auto-absorption made here is not a new one. It was brought forward by Stark (*Phys. Zeitsch.*, **8**, 81 (1907)) in order to explain some of his results on fluorescence, and also by Bruninghaus (*Le Radium*, **8**, 147 (1911)) in the case of some cathodo-phosphorescence phenomena.

[3] *Phys. Rev.*, **22**, 566 (1923).

platinocyanide is $(2{\cdot}12 \pm 0{\cdot}01) \times 10^{-7}$ second, and $(2{\cdot}12 \pm 0{\cdot}14) \times 10^{-8}$ second with rhodamine. This, however, is not all that is required, the question being what is the rate of growth of the fluorescence of some such compound as a uranyl salt, where the rate of decay has been accurately determined and where only one band group is concerned.

Cathode Ray Excitation of Phosphorescence.—We may now consider the use of cathode rays as a means of exciting phosphorescence, and here we find a considerable extension of the field, since under the influence of this stimulation phosphorescence has been observed in many cases where it does not occur when the substances are exposed to light. An instance of this has already been given in the uranyl salts, which exhibit their characteristic fluorescence under stimulation by light and give the same emission, but with all the properties of phosphorescence, under the influence of cathode rays.

The first question which arises is the experimental technique, and this, in the main, is the same as that of any investigations involving the production of high vacua. This has been dealt with in some detail in Chapter II., and there is only one matter which requires special mention, namely, the design of the cathode ray tubes. As is

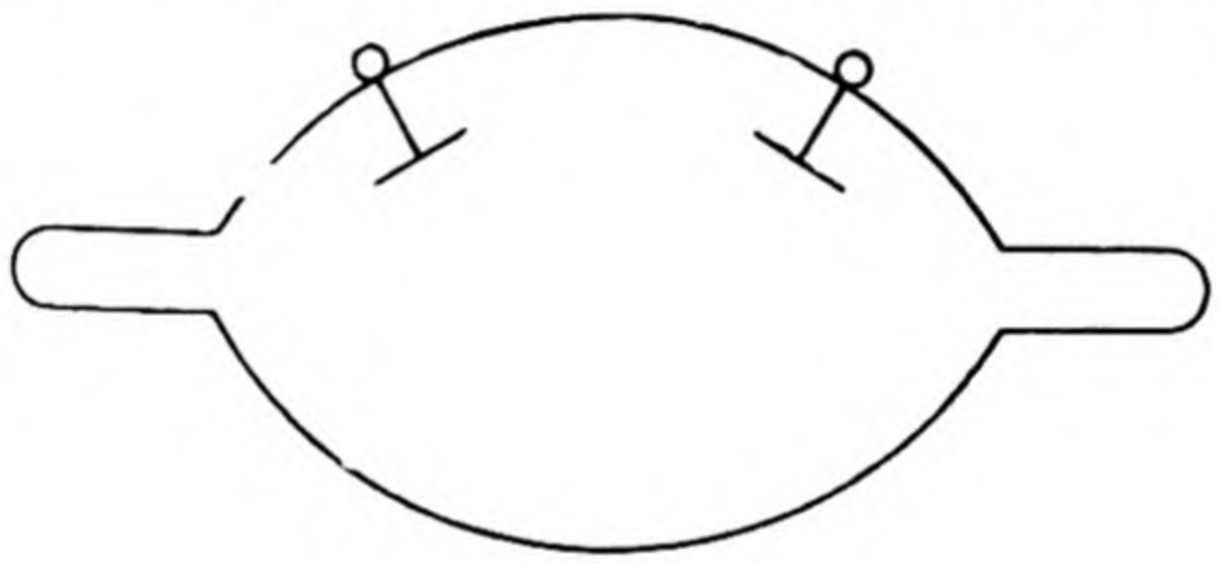


FIG. 85.

well known, Crookes was the pioneer in this field, and he mainly devoted himself to the phosphorescence of minerals and the rare earths. In his earlier work in which he was dealing with visible cathodo-luminescence he used a discharge tube, as is shown in Fig. 85. Since the paths of the electron streams are, in the main, straight and normal to the surface of the negative electrode, the thin flat electrodes shown in the figure are particularly well adapted to direct them on to the substance lying in the lower portion of the tube. In the exhaustion of these tubes, or, indeed, of any design of cathode ray tube used for the study of luminescence phenomena, it is necessary to carry it to a high stage.

It is advisable during the exhaustion carefully to heat the tube with a Bunsen burner in order to drive off the gas which is occluded upon the walls and in the substance to be excited. It will generally be found, if the exhaustion be carried first of all to a high point and the discharge made to pass, that a considerable quantity of carbon dioxide and hydrogen will at once be given up by the various parts of the tube. It is clearly necessary that all of this be removed before good results are obtained. This can be done with patience, by con-

tinually heating the tube and re-exhausting until no more gas is evolved. This can readily be tested by watching the effect of further heating upon the appearance of the discharge; no effect, of course, should be produced. As regards the extent to which these tubes must be exhausted, this must be judged for each separate tube. It will be found that the phosphorescent effect will, during the exhaustion, steadily improve until a maximum is reached, after which it will begin to decline; the degree of exhaustion at which the maximum occurs differs with different tubes. In connection with the use of these tubes, it must not be forgotten that many minerals tend to give up gases under the influence of the rays, due to the heating, etc. Care should, in such cases, be taken only to run the discharge for a very short time; if, however, it is required to make a lengthy observation, it is advisable to leave the tube in connection with the pump, so that any gas which is evolved can at once be removed.

In his later work, Crookes found it necessary to examine the emission in the ultra-violet region of the spectrum, and therefore it became necessary to alter the design of the vacuum tube so that the

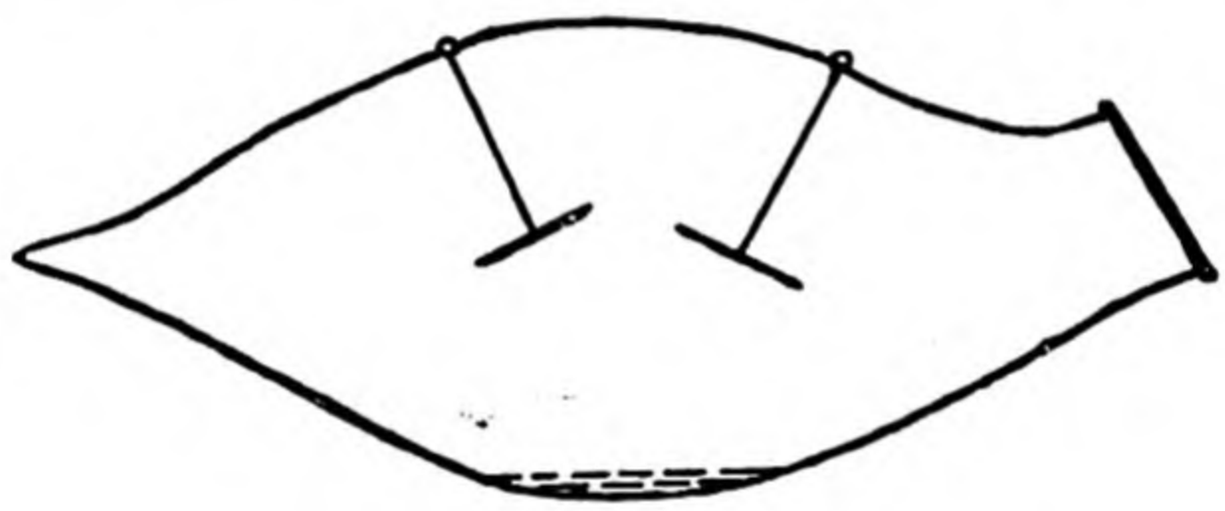


FIG. 86.

phosphorescent material could be viewed through a quartz window. A diagram of such a tube is shown in Fig. 86.

Urbain [1] has devised forms of tubes which are excellently suited for the observation of phosphorescence. When it is not required to examine the ultra-violet luminescence, the form of tube is used, as shown in Fig. 87, in which a ground glass joint connects the lower portion of the tube containing the substance to be examined. The anode is made in the form of a ring, while a slightly concave surface of aluminium forms the cathode. Owing to the fact that the cathode streams pass through the annular anode, they are very closely bunched together, and, therefore, the ground joint is protected from their bombardment, and they strike the substance which is placed in the bottom of the lower tube. The great convenience of this apparatus is that the lower tube can readily be removed, cleaned and primed with a fresh substance. Urbain has introduced a slight modification for use when the ultra-violet phosphorescence is to be examined. The lower tube is then made in the shape shown in Fig. 88, the substance being heaped up in the angle of the tube, and the phosphorescence examined

[1] *Ann. de Chim. et Phys.*, **18**, 222 (1909).

through the end of the tube, which is closed by a quartz plate. Urbain has also devised an arrangement in which a number of these tubes are united together in one apparatus. This is shown in Fig. 89, which is shown in plan and also end elevation. In this apparatus

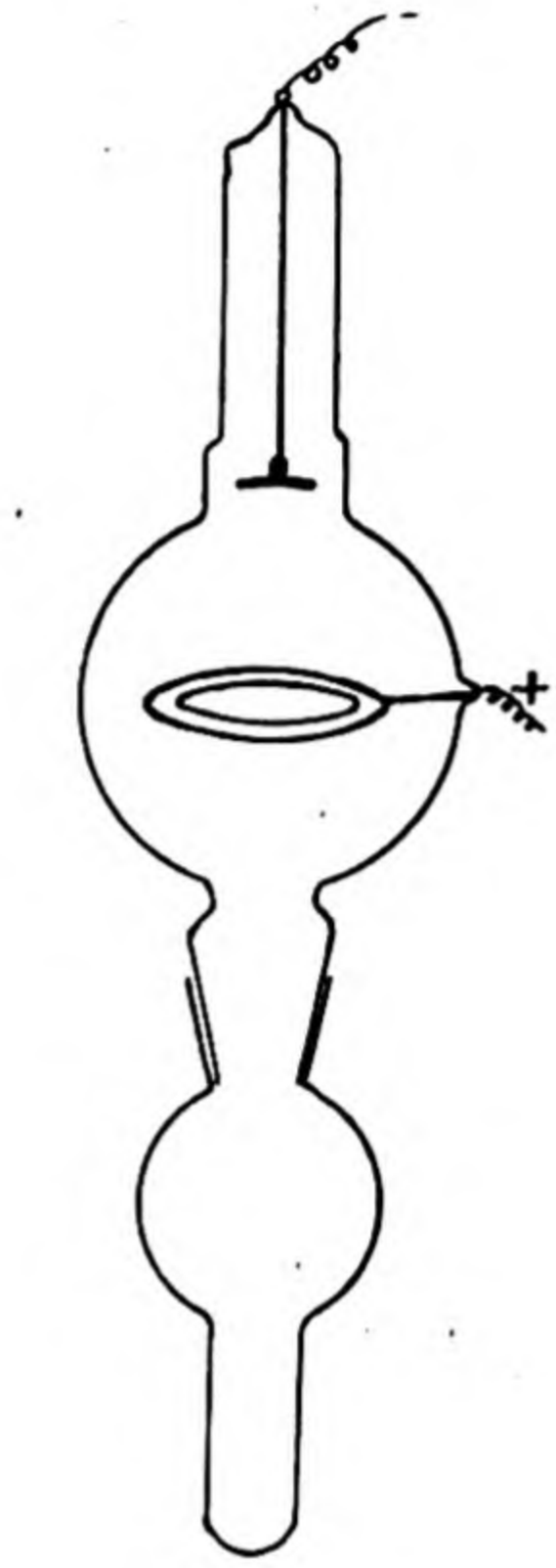


FIG. 87.

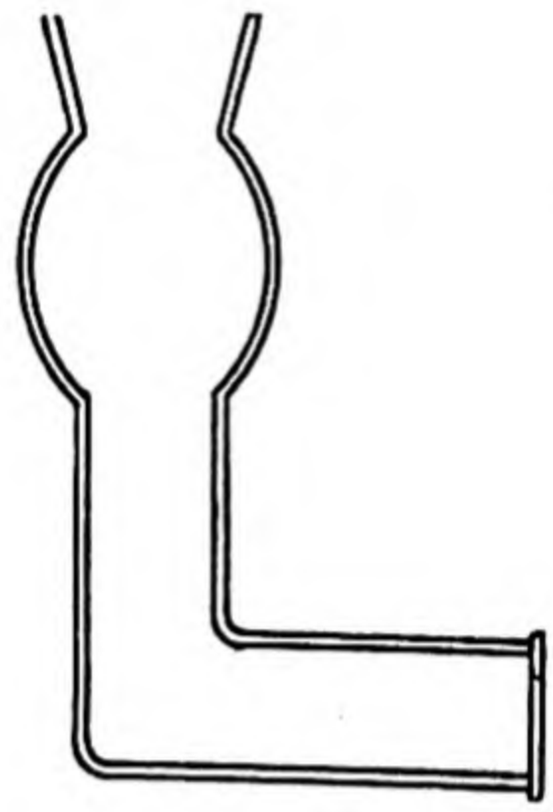


FIG. 88.

the anode is a long wire passing the complete length of the upper glass tube, whilst each observation tube carries its own cathode. When in use all the cathodes are joined together, so that the apparatus is exceedingly well suited for a comparison between the phosphorescence of different substances such as occur during the fractionation

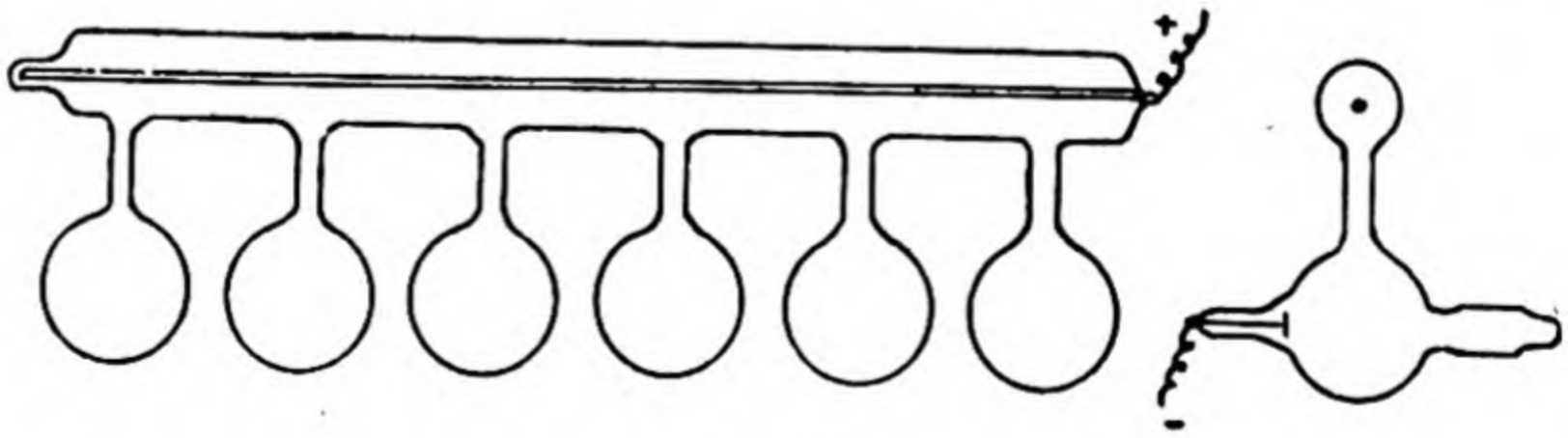


FIG. 89.

of the rare earths, when it is necessary to follow the fractionation process with spectroscopic observations in order to see how it is progressing. The advantage of the arrangement lies in the fact that each of the materials are made to phosphoresce under as nearly as possible the same conditions.

These few designs will suffice to indicate the general principle on which these tubes are constructed. Many minor modifications have been introduced from time to time in order to secure a particular advantage for a particular purpose, but these cannot be specified. Mention may, however, be made of the investigation of phosphorescence at very low temperatures, since in this case the discharge tubes must be so made that the substance under investigation can be cooled. A design very suitable for this purpose is that shown in Fig. 87, it being only necessary to immerse the lower end containing the substance in the liquid air or other cooling agent.

The early work of Crookes on the phosphorescence excited by cathode rays has already been referred to. At first this consisted in a study of the brilliant colours exhibited by many naturally occurring minerals, and then at a later date he devoted himself to the phosphorescence of the rare earths. The chemistry of these elements and their separation from one another had for a long time been a subject of great interest to him, and he was the first to recognise the value of their phosphorescence in this work. It must, of course, be remembered that at that time little or nothing was known of the phenomenon except as regards its stimulation, since it was before the days of Lenard and Klatt and of Urbain and Bruninghaus. The conclusions that Crookes drew, though in part correct, suffered from his want of knowledge of the effect of concentration. He investigated the phosphorescence spectra of the rare earths and the manner in which these changed as the mixtures were fractionally crystallised or precipitated according to the chemical methods in use at that time. He was led to the view that each phosphorescence emission band is characteristic of a single rare earth element, and further, that the intensity of an emission band gives an indication of the amount present of the relevant element. It was this latter conclusion which was incorrect, and on one occasion it led to a very surprising result. Pursuing a method of fractional separation which it was believed would lead to the preparation of a pure specimen of a particular rare earth, the stage was reached at which a reasonable high state of purity was expected. The product, however, showed no phosphorescence. This result was somewhat astounding on the view that the phosphorescence band seen in the early stages was characteristic of the rare earth and had an intensity proportional to its concentration. As was subsequently pointed out by Urbain, the phenomenon was exactly that to be expected from the fact that no pure substances phosphoresce.

Mention has already been made of Urbain and Bruninghaus' work [1] on cathode rays phosphorescence in which they extended Lenard and Klatt's conclusions drawn from observations of photo-phosphorescence. In their paper Urbain and Bruninghaus state their conclusions in a more definitive manner than did Lenard and Klatt. These are as follows :—

[1] *Ann. Chim. et Phys.*, **18**, 293 (1909).

1. Pure substances do not show any phosphorescence.

2. Phosphorescence is only shown by a mixture of at least two substances.

3. Phosphorescence is more especially a property of diluted matter.

4. In all cases when a mixture of two substances shows phosphorescence, one acts as the diluent for the other which is the active principle, and is named the phosphorogen.

5. In such a binary mixture there always exists an optimum of phosphorescence which corresponds to a very small quantity of the phosphorogen.

6. This law of optimum is quite general, being applicable to all phosphorescing substances.

The significance of these conclusions in any work on the rare earths is manifest, and it is quite obvious that the phenomenon of phosphorescence cannot be used as a test of purity, but it still can, and does, render great aid in this work. It is common knowledge that this field of chemistry owes more than a little to Urbain, and he has shown very clearly how serviceable a handmaiden phosphorescence can be on occasion. Let us picture a particular mixture of rare earths for which a promising method of fractional separation has been worked out. For the benefit of those who have not had experience of the tediousness of such fractionation it may be pointed out that a fractionation process, at best, depends on minute differences in solubility of a particular salt, with the result that a very long series of operations is necessary, each of which achieves just a small alteration in the composition. To this it may be added that the atomic weights or equivalents of the pure elements composing the mixture differ but little from one another. It is convenient to number the fractionation operations for purposes of recognition, and at intervals in the long process the equivalents of the fractions are determined. These values are plotted against the numbers of the fractions and in the early stages a smooth curve is obtained. After a time, however, inequalities begin to make their appearance, which, if the experimenter is fortunate in his choice of method, develop into straight lines parallel to the number axis. This means that fractions of constant composition are obtained, unchanged by repeated fractionation. These fractions may either be pure salts of a single rare earth or mixtures of constant composition analogous to mixtures of constant boiling-point, that is to say, they are unaffected by further fractionation. It is at this stage that phosphorescence can be called in aid, since in the one case the material is a pure substance and in the other it is a mixture. If the rare earth oxide prepared for the material exhibits phosphorescence, it certainly is a mixture, whereas if no phosphorescence is shown it is very probably a single pure substance.

It must be pointed out that the whole of Urbain and Bruninghaus' conclusions are not universally true. In the first place, Nichols and his co-workers have shown that the purest possible uranyl salts exhibit brilliant phosphorescence with a persistence of many minutes

when stimulated by cathode rays. There is no possible question here of the luminescence being due to an impurity, since it is true for different salts and the wave-lengths are identical with those of the fluorescence excited by light. In the second place, their first conclusion as to the phosphorescence of a pure substance can only be generally true in the restricted sense of phosphorescence with visible persistence. Many cases are known of pure salts which do not exhibit this slow emission immediately after excitation, but store up the exciting energy and produce a metastable activated state with a latent power of phosphorescence which reveals itself on heating. A wrong impression would be gained if these conclusions were accepted as being rigidly true for all substances and the term phosphorescence were not strictly defined.

This divergence is not very satisfactory, but it is due to the fact that Urbain based his conclusions on the results obtained in the investigation of rare earth phosphorescence. This much is obvious from the generalisation he made in the sixth conclusion given above. It was emphasised by Nichols in his work on the uranyl salts that the existence of a crystalline state is essential for the causation of certain luminescence phenomena, these not being given by mere solid solutions. This would also seem to be the explanation of the fact that a preliminary heat treatment is necessary in the preparation of active phosphores, the heat treatment inducing the formation of a crystalline structure. In all probability the rare earth oxides are amorphous in the pure state, and hence do not exhibit the phosphorescence phenomena characteristic of pure crystalline substance. It becomes of great importance, therefore, to remember that the physical state of the substance is a very definite controlling factor in phosphorescence phenomena, and that this is particularly true of pure substances. Any general statement of the luminescence properties of pure substances must be associated with information as to their physical state.

It has already been mentioned in discussing Lenard and Klatt's work that they made many observations of the phosphorescence exhibited by their phosphores at the temperature of liquid air. Reference was also made to Nichols' investigations of the luminescence of the uranyl salts at — 185°. A considerable amount of other work has been carried out both on the photo-luminescence and the cathodo-luminescence of substances at this low temperature. In connection with this work it must be remembered that, apart from the major influence of the low temperature in establishing the conditions suitable for luminescence, low temperatures tend to resolve a broad emission band into its component sub-groups. This was discovered by Becquerel and Onnes, and discussed with particular reference to uranyl salts on p. 268.

We may, in passing, refer to the fact that the constant wave-number relation between the sub-groups, so well established for fluorescence spectra by Nichols, is equally true for phosphorescence emission bands where these have been resolved. One instance of this

may be given here, and certain others will be detailed below. As the present instance we may take the phosphorescence band of samarium oxide which is excited by cathode rays when calcium oxide is the diluent.

This emission band was studied and measured by Howes.[1] The oxide was dissolved by hydrochloric acid and diluted to 1/100, and this solution was added to pure calcium carbonate in the proportion of 1 atom of samarium to 125 atoms of calcium. The mixture was evaporated to dryness with stirring, and portions of the residue were heated in glazed crucibles at several temperatures between 200° and 1200° in an electric resistance furnace. The duration of the heat treatment was also varied at each temperature between one and three hours. It was found that a critical temperature of about 600° was necessary to render the luminescence sufficiently intense for spectroscopic observation. The duration of the heat treatment was found to be without influence. About twenty different preparations were made in this way, and finally, one specimen was heated for five minutes in the core of one of the carbons of an arc. It was observed that the preparations which had been heated to 1200° or higher gave the most brilliant luminescence at 20°.

The spectrum consists of about thirty narrow bands of different intensities, the wave-numbers of which can be arranged in nine series of constant difference. The position of these bands is in no way shifted, whether the specimen is heat-treated at 600° or 3000°. The measurements are given in Table LXIV., the series being designated by *a*, *b*, *c*, *d*, *e*, *f*, *g*, *h*, and *i*, respectively.

TABLE LXIV

Wave-length.	Wave-number.	Series.	Wave-length.	Wave-number.	Series.
6801	1470	*c*	5898	1695	*g*
6734	1485	*d*	5868	1705	*d*
6643	1505	*e*	5793	1726	*e*
6600	1515	*a*	5757	1737	*a*
6536	1530	*f*	5721	1748	*f*
6470	1546	*b*	5675	1762	*b*
6405	1561	*h*	5653	1769	*i*
6329	1580	*c*	5621	1779	*h*
6270	1595	*d*	5581	1792	*c*
6183	1617	*e*	5553	1801	*g*
6146	1627	*a*	5550	1812	*d*
6140	1629	*a*	5481	1824	—
6103	1639	*f*	5451	1835	*e*
6050	1653	*b*	5416	1846	*a*
5990	1669	*h*	5387	8156	*f*
5940	1684	*c*	5328	1877	*i*

[1] *Phys. Rev.*, **17**, 60 (1921).

Returning once again to the investigations of luminescence at low temperatures, we may note that von Kowalski [1] found that alcoholic solutions of the nitrates of the rare earths, when cooled to — 185° and excited by the rays from a mercury lamp, exhibited true phosphorescence. In this case the diluent is the alcohol, the solution becoming a glass-like solid at the low temperature. The phosphorescence emission in many cases persisted for five minutes after the exciting light was cut off. It was also found that alcoholic solutions of phenanthrene, anthracene, and anthraquinone, when cooled to — 185°, developed persistent phosphorescence. In all these cases the emission bands were resolved into fine bands or lines.

In a later paper von Kowalski [2] gives a complete account of his investigations on the phosphorescence of organic compounds and prefaces this with an abstract of a very extended research into the same subject by Borissow.[3] The conclusions which Borissow drew from his results may be given, as his paper is somewhat inaccessible.

1. The phosphorescence of organic compounds at — 185° is a widespread phenomenon, relatively few showing no luminescence.

2. Visibly coloured organic compounds rarely phosphoresce; thus the nitro-compounds and the dye-stuffs do not exhibit any luminescence. On the other hand, solutions of some coloured compounds, *e.g.* fluorescein and rosaline, give an intense phosphorescence, the pure substances being non-luminescent.

3. The organic acids, albumin, and some of the alkaloids show more intense phosphorescence than other solid compounds.

4. The most usual colour of the phosphorescence is green.

5. The persistence of the phosphorescence is independent of the time of excitation, provided that this is longer than one second.

6. The effect of temperature on the persistence was investigated with twenty-six compounds, and in fifteen of these it was found to be a linear function of the temperature.

7. Increase of temperature changes the colour of the phosphorescence to white and then to a bluish shade.

8. The intensity and persistence decrease with rise of temperature.

9. Alcoholic and aqueous solutions of compounds phosphoresce more strongly than do the compounds themselves.

10. Change in concentration has little effect on the intensity, persistence, or colour of the phosphorescence.

Von Kowalski states that his results are not in complete agreement with the foregoing conclusions of Borissow. He points out that the phenomenon is very largely influenced by the presence of impurities, and, indeed, that in some cases the phosphorescence observed is entirely due to impurities. He gives as an instance methyl alcohol, which, when absolutely pure, shows no trace of phosphorescence when cooled to — 185°. If, however, this pure specimen

[1] *Comptes Rendus*, **145**, 1270 (1907). [2] *Phys. Zeitsch.*, **12**, 956 (1911).
[3] *J. Russ. Phys. Chem. Soc.*, **37**, 249 (1905).

is exposed to air at room temperature for an hour, it gives definite evidence of phosphorescence after cooling for a second time.

He shows that without any doubt there is in the case of solutions an optimum concentration for phosphorescence, which, with alcohol as the solvent, is about 0·05 molar. It is very important to note that the activating light has at times a very definite influence on the phosphorescing substance. For example, the colourless alcoholic solutions of the hydroxyphenols, aminophenols, diphenylamine, etc., on exposure to ultra-violet light at — 185°, develop a visible colour. When the frozen solutions are warmed until they melt, the colour vanishes.

The first part of von Kowalski's work consisted of a series of qualitative investigations of the phosphorescence. The activation period was, in each case, fifteen seconds, and the light source was a quartz mercury lamp. The results are chiefly connected with the effect of the chemical nature of the substances and need not be detailed here.

The second, and from the present standpoint more important, part of the investigation, dealt with the phosphorescence emission in greater detail on the quantitative side. In the first place, the phenomenon shows an analogy with the cathode ray phosphorescence examined by Goldstein, in that there exist two stages. If the substance is illuminated only for a short time (0·1 to 0·25 second depending on the particular substance) the phosphorescence shows a continuous spectrum. In some cases differences of intensity are visible in different regions of the spectrum. This emission has a very small persistence, and appears to correspond to the instantaneous bands of Lenard and Klatt. The colour changes during the decay, the long wave end disappearing before the short wave end.

If the time of excitation is increased to more than one second, narrow phosphorescence bands begin to appear in the continuous spectrum of the instantaneous phosphorescence. The intensity of these bands increases with the time of excitation until it asymptotically reaches a maximum value. These bands are called the progressive phosphorescence, in order to differentiate them from the instantaneous phosphorescence. The two are due to different causes, since after the instantaneous phosphorescence has disappeared the bands of the progressive phosphorescence remain clearly defined. The difference between the two is emphasised by the fact that the persistence of the former is scarcely altered by change of temperature, whilst that of the latter is markedly changed, becoming greater with fall of temperature. It may be noted in passing that no phosphorescence of any kind is observed above — 145°.

Von Kowalski gives the measurements of the wave-lengths and wave-numbers of the bands observed with thirty compounds, and compares these with the fluorescence emission given by the same compounds at ordinary temperatures. Whilst these need not be given in detail, it is interesting to note that the phosphorescence emission

in each case takes place at longer wave-lengths than those of the fluorescence. It would seem that in the majority of cases the phosphorescence bands characteristic of each substance can be arranged in series of constant wave-number difference. This is shown by von Kowalski to be the case with benzene, where two such series exist, as shown in Table LXV.

TABLE LXV.

PHOTO-PHOSPHORESCENCE OF BENZENE.

1/λ.		1/λ.	
230		233	
	9		9
239		242	
	10		10
249		252	
	11		11
260		263	
	10		11
270		274	
	10		10
280		284	
	9		11
289		295	

The phosphorescence of organic compounds at — 185° has also been studied by Goldstein,[1] who made use of cathode rays as the exciting agent. He found that when aromatic substances are cooled in liquid air and exposed to cathode rays there are evidenced three spectra in succession. He called these the initial spectrum, the chief spectrum, and the solution spectrum respectively. All three spectra are characteristic of a particular substance, the second being more especially so, and it is possible to recognise this chief spectrum of many compounds of the aromatic series. The solution spectrum is a true phosphorescence effect which is due to the presence of impurities, and it is an extraordinarily delicate test of such contamination. For example, he was able to detect the presence of less than 0·001 per cent. of naphthalene in a sample of methyl benzoate.

The chief spectrum appears to be characteristic of the substance present and to correspond to the so-called progressive phosphorescence of von Kowalski. It is somewhat remarkable that this cathode ray phosphorescence is always situated nearer the red than the photo-phosphorescence, this being in its turn, as already stated, nearer to the red than the ordinary fluorescence obtained at room temperature. The cathodo-phosphorescence is also resolved into narrow bands like the photo-phosphorescence. Two examples are given in Table LXVI.

[1] *Deutsch. phys. Ges., Verh.*, **6**, 156, 185 (1904); **12**, 376 (1910); **13**, 378 (1911); **14**, 33, 493 (1912); *Phys. Zeitsch.*, **13**, 577 (1912).

which show the different spectral regions in which the three phenomena make their appearance, the measurements being expressed in wave-numbers.

TABLE LXVI.

PARA-XYLENE.

Cathodo-phosphorescence.	Photo-phosphorescence.	Fluorescence.
176	234	294
180	239	to
184	243	364
188	249	unresolved
192	253	
196	258	
200	265	
205	270	
208	273	
212	282	

ORTHO-XYLENE.

185	242	298
188	246	to
190	250	370
192	257	unresolved
195	261	
198	265	
200	272	
202	277	
205	281	
—	287	

Lastly, it will be seen that the bands of the cathodo-phosphorescence form series of constant wave-number difference.

Flame Excitation of Luminescence.—It is well known, as has already been stated, that there is an upper temperature limit above which neither phosphorescence nor fluorescence as ordinarily understood can evidence itself. In certain cases, however, it is possible to detect traces of luminescence when the temperature is approaching that of dull red heat, and the study of one of these instances led Nichols and Wilber [1] to the discovery of a new phenomenon, namely, the excitation of luminescence by means of the hydrogen flame. The first observations of this phenomenon were made with air-slaked lime which were found to emit a yellowish-green glow when heated directly in the hydrogen flame. Nichols and Wilber were able to prove that the phenomenon is not one of ordinary temperature radiation and that it occurs only within a narrow range of temperature, within which it rises to a maximum and disappears. The lumin-

[1] *Phys. Rev.*, **17**, 453 (1921).

escence is not producible by heating the substance electrically, as on a strip of metal, nor by radiation or conduction as in a furnace; when a flame is employed the glow occurs only within the flame.

In the case of substances which exhibit this phenomenon and also photo-luminescence, the lower temperature limit of the former is often, but not always, above the upper temperature limit of the latter. Moreover, the active range of temperature extends above that at which thermoluminescence takes place.

It was also found that by no means all flames are capable of exciting this luminescence. Indeed, the hydrogen flame, and to a less extent the flames containing hydrogen, such as the colourless flame of coal gas, seem to be the only ones which are effective. The flames of burning alcohol, ether, and carbon bisulphide are quite inactive in this respect. The active region of the hydrogen flame is the outer portion of the reducing zone.

In order to measure the temperature under which luminescence takes place, the substance under investigation was placed, in the form of a fine powder, on one of the end faces of a cylinder of copper 30 mm. in diameter and 20 mm. thick. In a narrow slot cut in this face was placed a platinum wire and the copper was hammered on to the wire so as to make it a part of the surface. This formed one junction of a thermo-electric element by means of which the temperature was measured, the electromotive force of such a junction at known temperatures having been previously determined.

Nichols and Wilber considered very carefully the possible temperature difference between the copper block itself and the outer surface of the powdered substance on the block. They satisfied themselves that in most cases where the precise temperature was in question this temperature difference was small.

In general, the temperature measurements were made with the copper block heated by an electric furnace or a Bunsen flame. The mass of the block and its thermal conductivity were so large that no measurable rise in temperature took place when the small hydrogen flame was applied from above on to the powder. This was confirmed by observations of the heating power of the flame on layers of black oxides, the radiating power of which enabled the temperature to be determined directly by means of a Morse pyrometer. It was concluded that with the thicknesses of powder used the temperature of the copper coincided with that of the luminescent powder to a sufficient degree of accuracy.

One of the earliest views was that the luminescence involved ionisation phenomena or the production and movement of charged particles. In order to test this, electrostatic fields were applied with their lines of force at times transverse to, and at other times parallel to, the stream lines of the flame. Although potential differences of many thousand volts were used no effect whatever was produced. In seeking for an explanation of the phenomenon the possibility suggested itself that the excitation was due to ultra-violet radiation

within the flame itself. With the view of testing this, the substances which exhibit this flame luminescence were suspended within the path of the discharge of a mercury arc lamp. These substances remained completely unaffected, whereas a synthetic ruby under the same conditions glowed with great brilliance until it reached the upper temperature limit when the luminescence suddenly was extinguished. It would seem highly improbable that any photo-excitation of the hydrogen flame could be as intense as that of the mercury arc discharge.

On the other hand, it was proved that the luminescence is actually due to the hydrogen flame, that is to say, the excitation is due to the combustion of the hydrogen with oxygen. A glass tube about 1 cm. in diameter and 20 cm. in length was attached to the nozzle of an oxy-hydrogen blast lamp, and a small amount of calcium oxide was evenly distributed over the inner walls of this tube. When a stream of hydrogen was passed through the glass tube and ignited at the open end, there was no excitation of the line even though the tube was externally heated to redness. The admission of air through the oxygen intake also produced no effect, whatever the temperature of the lime, until the supply of air was sufficient to cause the flame to strike back, and when this took place the progress of the flame through the tube could be traced by the luminescence of the oxide. By adjustment of the supply of air the zone of combustion could be brought to rest within the tube, when its position was clearly marked by a narrow ring of luminescent oxide. This experiment clearly proves that the luminescence is only in the zone where the actual reaction between hydrogen and oxygen is taking place. Certain modifications of the experimental details proved further that the active zone of the flame was equally sharp and well-defined whether a jet of hydrogen was burning in oxygen or a jet of oxygen in hydrogen. The luminescence always took place within the hydrogen next to the boundary between the hydrogen and oxygen. Further experiments gave evidence which was against the view that the presence of atomic hydrogen or of triatomic hydrogen is the origin of the luminescence.

Before proceeding to a detailed description of the luminescence phenomena a word of caution may be uttered against the acceptance of the failure of the mercury arc to excite the radiation as a definite proof that the phenomenon is not one of photo-excitation by the radiation from the hydrogen flame. There remains the possibility that the radiation from the mercury arc is not of the correct wave-length to excite the substances, in which case, of course, no glow would be seen. The brilliant luminescence shown by the synthetic ruby in the mercury arc lamp is proof enough that, given the right conditions, photo-excitation can be set up by this discharge, and this strengthens the view that the failure in the mercury lamp of those substances which luminesce in the hydrogen flame is due to their exciting wave-lengths not being the same as those radiated by the mercury arc. Then again, support for this view is found in the re-

markable fact that the flame of burning gaseous hydrogen is essential for the observation of this most interesting phenomenon.

The following substances were found by Nichols and Wilber to be sensitive to flame excitation :—

1. Calcium oxide, and also the oxides of magnesium, zinc, aluminium, silicon, and zirconium.

2. Certain phosphorescent sulphides, such as Sidot blende, and sulphides of the Lenard and Klatt type. Not all of the latter are sensitive, only twelve being found to respond strongly to flame excitation out of forty-four which were tested. A few others showed a feeble effect.

3. White sapphires, corundum, synthetic rubies, calcite, fluorite, kunzite, boric acid, telluric acid, and very pure specimens of cadmium phosphate, calcium carbonate, calcium sulphide, and zinc sulphide, all incapable of photo-excitation at ordinary temperatures.

On the other hand the following were found to be inert :—

4. All dark substances, such as the oxides of copper, lead, iron, nickel, cobalt, manganese, cadmium, tungsten, etc.

5. The oxides of strontium, barium, antimony, bismuth, erbium, cerium, lanthanum, and thorium.

6. Materials from a freshly-ignited Welsbach mantle and from a Nernst filament.

7. Specimens of uranium glass, didymium glass, fused quartz, etc. Calcium tungstate, one of the most brilliant phosphorescent substances under the influence of X-rays, and artificial Willemite, which is perhaps the brightest of photo-luminescent bodies, are quite inert in the hydrogen flame.

The nature of the flame luminescence and the temperature limits may now be described.

Calcium oxide, whether prepared from slaked lime, calcite, or metallic calcium, gives a strong yellow glow, and the temperature range is the same with all the different preparations. The luminescence spectrum consists of two or more overlapping bands, one of which in the red-yellow makes its appearance at a lower temperature than the other and vanishes at about 670°. The second band, which is yellow-green, becomes visible at higher temperatures, and does not entirely disappear until the temperature reaches 725°.

Zirconium oxide gives a pale blue-green luminescence, commencing very definitely at 76° and vanishing at 372°. On raising the temperature to 440° a deep ruby-red luminescence makes its appearance, and this disappears at 720°.

Silicon oxide, whether in the precipitated form, or as a coating deposited by the vapour from the silicon arc, shows the pale greenish-white luminescence. The lower temperature limit of 85° is very sharp and definite, the upper limit being 367°.

Aluminium oxide is notable for the low temperature at which the luminescence makes its appearance. The glow is pale green in colour and has the temperature limits of 52°-692°. This is true for

amorphous and crystalline alumina. A synthetic ruby was found to give a green luminescence without any trace of the well-known deep red photo- and cathodo-luminescence. A synthetic sapphire gave a similar pale-green flame luminescence, although it also exhibited a red phosphorescence when excited by cathode rays.

Magnesium oxide gives a fine white flame luminescence with the temperature limits of 76°-680°. At higher temperatures a second blue-violet luminescence appears, the exact temperature conditions of which were difficult to determine. Zinc oxide also shows two stages of flame luminescence, but the lower stage is somewhat difficult to excite. It is intense red in colour and begins at 568°, and at 704° it changes into the second stage, which is characterised by a blue-green glow and persists up to 948°. The latter stage is brilliant and is so strikingly different from the temperature radiation on which it is superimposed, that it can be quantitatively studied.

The phosphorescent sulphides differ from the above-mentioned oxides in that they are strongly photo-luminescent at ordinary temperatures. They are usually excited by the ultra-violet radiation from the hydrogen flame, even at a considerable distance. When warmed by the radiation from the flame, though not in contact with it, they show thermo-luminescence, and then, having lost the power of photo-excitation, they show flame luminescence on being brought into the active zone of the flame and heated to the proper temperature. It is of great interest to note, as will be shown below, that the spectrum of the flame luminescence contains the same groups of narrow bands as the spectrum of the photo- or cathodo-luminescence. It is also of interest that, whereas the phosphorescence is generally attributed to the presence of an active material in solid solution in the diluent, this is not essential for flame excitation. A sample of zinc sulphide, which was so pure that it did not respond to the radiation from the iron spark, gave a brilliant yellow-green glow at a red heat in the flame. This luminescence became visible at 560°, and at 616° was more intense than that given under the same conditions by specimens of Sidot blende which had been specially prepared to show phosphorescent properties. The same sample of pure zinc sulphide responded strongly to cathode ray excitation at ordinary temperatures, there being, however, no persistent after-glow.

Pure calcium sulphide is inert under photo- and cathodo-excitation, but gives a flame luminescence through an unusually wide range of temperature. A bluish-green glow commences at 60° and increases in intensity as the temperature is raised. At about 330° the colour changes somewhat suddenly to a bright yellow and this persisted with first increasing and then decreasing intensity until at about 737° it disappears. On cooling, the same phenomena were observed in the reverse order, the maximum intensity of the yellow glow being visible at about 500°. It is to be noted, however, that the colour and upper temperature limit of the second stage are very similar to those of calcium oxide.

The spectra of the flame luminescence given by several substances were examined by Howes.[1] They consist in general of broad bands which can, by spectrophotometric observations, be resolved into narrow components, and these components form series with constant frequency differences. A fundamentally important fact discovered by Howes, to which reference has already been made, is that when the same substance responds to both photo-excitation and flame excitation the spectrum given in each case consists of the same narrow components. Since the relative intensities of these components are not the same in the two spectra the envelope intensity curve of the composite band is not the same in the two cases. Howes gives in his paper four instances, namely, air-slaked lime and three of the Lenard and Klatt phosphorescent sulphides.

As already described, the flame luminescence of the lime is of an orange-yellow colour and this is very similar in appearance to the photo-luminescence of natural calcite when excited by the radiation from the iron spark. The broad band can be resolved into eleven narrow components, which form two series with the same constant wave-number differences. These are set forth in Table LXVII.

TABLE LXVII.

LUMINESCENCE OF LIME.

Series A. Interval = 42.			Series B. Interval = 42.		
Flame excitation.	Photo-excitation.	Wave-number.	Flame excitation.	Photo-excitation.	Wave-number.
5975 A.	5977 A.	1673	6045 A.	6046 A.	1654
5833	5831	1715	5894	5896	1696
5689	5692	1757	5755	5754	1738
5563	5559	1799	5617	5618	1780
5432	5432	1841	5488	5488	1822
			5365	5365	1864

The shape of the envelope curve of the flame luminescence given by the lime corresponds more nearly to that of the calcite when photo-excited at 200° than at 20°, and this is not surprising since the temperature of the lime was about 350°. Although the temperature determines the relative intensities of the components, yet the A and B series are independent of both the temperature and the mode of excitation.

The spectrum of the photo-luminescence given by the Lenard and Klatt sulphide No. 3 (CaS, Bi, Na_4BO_4) when excited by the radiation from the zinc spark was studied by Nichols [2] and consists of a strong band in the blue and a broader but much weaker band in the orange.

[1] *Phys. Rev.*, **17**, 469 (1921). [2] *Proc. Amer. Phil. Soc.*, **55**, 496 (1916).

When excited by the hydrogen flame the orange band has a much greater relative intensity. Howes finds that this band can be resolved into narrow components which have the same position under both conditions of excitation as shown in Table LXVIII., one new band being observed in the flame luminescence.

TABLE LXVIII.

LUMINESCENCE OF CALCIUM BISMUTH SULPHIDE, NO. 3.

Flame excitation.	Photo-excitation.	Wave-number.	Interval.
6365 A.	—	1575	39
6208	6200 A.	1614	39
6048	6049	1653	39
5912	5910	1692	39
5785	5781	1731	39
5650	5650	1770	39
5530	5528	1809	39
5415	5411	1848	39
5300	5300	1887	—

The same similarity between the spectra of the flame luminescence and the photo-luminescence was observed with Lenard and Klatt's strontium bismuth sulphide, No. 13, and the measurements of the band components are given in Table LXIX.

TABLE LXIX.

LUMINESCENCE OF STRONTIUM BISMUTH SULPHIDE, NO. 13.

Flame excitation.	Photo-excitation.	Wave-number.	Interval.
5565 A.	5562 A.	1793	58
5414	—	1851	58
5235	5238	1909	58
5080	—	1967	58
4938	4938	2025	58
4800	4801	2083	58
4668	4670	2141	58
4546	4547	2199	58

In a second paper Nichols and Wilber[1] deal with the cathodo-luminescence of the thin films of the oxides which exhibit the phenomenon of flame luminescence. These films were prepared by sublimation in the electric arc and were found to have the following properties in common:—

[1] *Phys. Rev.*, **17**, 707 (1921).

1. They are not photo-luminescent at ordinary temperatures.

2. They luminesce under cathode bombardment at temperatures far above those at which, in general, photo-luminescence becomes extinct.

3. They are all capable of flame excitation as well as cathode excitation.

4. In their behaviour they are to a great extent independent of the source from which they are obtained, though this is not a universal characteristic.

5. None of the oxides thus prepared show notable persistence phosphorescence, although most of them with small admixtures of chromium, manganese, or bismuth may, by suitable heat treatment, be rendered strikingly phosphorescent.

From observations of the cathodo-luminescence at various temperatures it was found that the upper temperature limit is the same as that of the flame luminescence. It was further noted that the colour of the luminescence changes as the temperature rises, and Nichols and Wilber proved that this is due to the alteration in the relative intensities of two closely situated, partly overlapping bands, the more refrangible band being the more enhanced by increase of temperature. This phenomenon is not new, having been observed by Wiedemann and Schmidt and previously to them by Goldstein and by Crookes. No variation whatever was found in the wave-lengths of the bands with change of temperature, which confirms Lenard and Klatt's original observations. Some experiments on the effect of pressure in the discharge tubes showed that marked changes in the relative intensities of the bands are produced by altering the pressure, with the result that the luminescence has different colours at different pressures. The relative intensity of the band of longer wave-length is increased as the pressure is diminished.

In concluding this descriptive account of the phenomena of luminescence I would say that it has been restricted to those investigations which seem to be the most important from the two points of view—experimental methods and value of the results obtained. Selection out of a great wealth of material is always a difficult matter in writing a reasonably short account of a branch of scientific work, and it is always open to criticism, since it must inevitably be determined by personal views. Whilst possibly some apology is needed for the two sins of omission and commission, more may be needed for the following section in which an attempt is made to find a theoretical explanation of all the cognate phenomena we have had under review.

A Theory of Fluorescence and Phosphorescence.—In the foregoing account of the more important work on fluorescence and phosphorescence no attempt has been made to deal with the theoretical side of the phenomena. It may indeed be said that in general this work has almost entirely been experimental, very few attempts having been made to offer a theoretical explanation of the observations. In fact there does not seem to have been brought forward any

satisfactory theory which accounts for the whole of the phenomena. There are, however, on record certain observations, some of which have not yet been referred to, that encourage me to believe in the possibility of formulating a theory which goes some way towards giving an explanation of one of the most interesting phenomena of spectroscopy. Whereas we have obtained as the result of the Bohr theory a completely satisfactory explanation of the line spectra emitted by elementary atoms, we are now concerned with the absorption and emission of energy of molecules, the majority of them very complex. The elementary theory of atomic emission spectra is simple enough, since, by the stimulus of the electric discharge or some similar exciting influence, one or more electrons are displaced from their normal orbits to new orbits, and the return of the electrons to their normal orbits is associated with the emission of definite radiations of light. The amount of energy radiated in any such simple process is the difference in the energy contents of the abnormal and normal states of the atom.

When molecular spectra are considered it is a known fact that under the same conditions of excitation as free atoms, molecules always emit band spectra which, by the work of Heurlinger, Lenz, and Kratzer, have been explained by the conception of molecular rotation. Each component line of a band spectrum is due to a jump from one rotational state to another and the radiated energy which gives the spectrum line is the difference in the energy contents of the two rotational states. The same explanation has been applied with success to the absorption bands exhibited by certain molecules such as the halogen hydrides and methane in the short wave infra-red region. This theory will be dealt with in Vol. III., Chapter IV., and there is no need to refer to it in greater detail at the present moment, except to say that it is believed by many that molecular rotation is the fundamental basis of all the selective radiation and absorption by molecules.

There exists in the fields of fluorescence and phosphorescence on the one hand and of absorption spectra on the other a great wealth of observed facts which do not seem susceptible of at any rate a simple explanation by the molecular rotation theory. I have been so far impressed by this that I have been led to believe that there must exist another mechanism whereby molecules can gain or lose energy, and that it is this mechanism which forms the basis of the luminescence phenomena we have had under review in this chapter.

If we consider as a whole the phenomena of molecular luminescence, it will be recognised at once that the complete mechanism consists in the stimulation of the substance by light, X-rays, or cathode rays, that is to say the absorption of energy by the molecules, and the radiation of that energy again at a different wave-length. In short, the molecules are raised to a state of higher energy content by the first process and return to their normal state of energy content during the second process, the total energy radiated being equal to

the difference between the two energy states. So much is obvious if we ignore the detailed mechanism whereby these two processes are achieved. Furthermore, we also must realise the fact that the second process, that is the radiation of the energy difference between the two states, may take place slowly or rapidly. On the one side we have instances where the emission of the energy persists for a very long time after the absorption of the energy has been stopped, and on the other side we have instances in which the radiation ceases instantaneously. As already explained at the commencement of this chapter the terms phosphorescence and fluorescence have been used to denote these two conditions respectively, the term fluorescence being applied only to those cases in which the luminescence ceases instantaneously after the excitation is stopped, that is to say when it has no measurable persistence. As the methods of measurements of this persistence were improved, more and more cases of fluorescence were found to have a finite persistence and so it became a question as to whether there were any real physical difference between the two. For this reason the whole of the phenomena were grouped under the name, first, of phosphorescence, and then, more recently, of luminescence. It would seem, however, that there are in fact two different processes depending on the difference in energy content of the two states, energised and normal, which may well be called, as in the early days, phosphorescence and fluorescence.

Let us consider a substance, the phosphorescence of which exhibits a long persistence, that is to say the emission of the absorbed energy is very slow. It is a well-established fact that if the substance be heated the phosphorescence increases in intensity and the time of persistence is shortened. In other words, the velocity of the emission is increased. The converse of this phenomenon has also been observed by Guntz [1] with a phosphorescent zinc sulphide which lost all luminescence on being cooled to —185°, but began again to glow when warmed. It is not surprising therefore to find substances which on activation are able to retain the absorbed energy for apparently an indefinitely long period without any measurable emission taking place. Such activated compounds are therefore in a metastable condition and it is very interesting that the phosphorescence emission may in such cases be initiated by the influence of heat or even by crushing them in a mortar, the former effect being known as thermoluminescence and the latter as triboluminescence.

It would seem, therefore, that we are justified in assuming the existence of two different energy states of the molecules as being necessary for the phenomena of fluorescence and phosphorescence, namely, the normal state and the activated state of greater energy content. The lower energy state is characterised by its power of selectively absorbing rays of light which convert it to the higher energy state, whilst the higher energy state is characterised by its power

[1] *Comptes Rendus*, **179**, 361 (1924).

of radiating energy, thereby returning to the lower energy state. This characterisation of the two energy states is shown clearly enough by Nichol's work on the uranyl salts and by the very numerous cases of fluorescence of organic compounds.

It may be thought that we are progressing over rapidly in assuming the static existence of two different energy states of the same molecules, for a separate existence of the higher energy state is necessary to explain the persistence of phosphorescence. It may be argued that this is a rather serious assumption to make at this stage when no evidence has been brought forward to support what is a somewhat novel proposition. On the other hand, there are a number of facts which have been observed at different times and which support this assumption very strongly, so strongly indeed that it seems to be the only possible explanation.

In the first place, reference may be made to the remarkable change in the physical properties of fused silica when it is exposed to ultra-violet light for a very long period.[1] It is well known that fused silica in layers of about 2 mm. thick is markedly transparent to ultra-violet light to as far as the wave-length 1900 A. If this material is exposed to the radiation from a quartz mercury lamp for some days, then, provided it is kept cool, the silica develops an amethyst colour exactly similar to that of natural amethyst quartz. Not only has the silica now developed a visible colour, but it has also become opaque to ultra-violet light of short wave-length. This new condition of the silica is metastable, and if it is heated to about 500°, or if it is crushed, it emits a brilliant green phosphorescence and returns to its normal colourless state which is transparent to short wave ultra-violet light. In this we find conclusive evidence of the existence of fused silica in two different states, a colourless state transparent to short wave ultra-violet light and a coloured state opaque to short wave ultra-violet light. We have, too, conclusive evidence that the coloured state has the higher energy content, since, apart from the fact that it is produced from the colourless state by the absorption of light energy, we have the incontrovertible fact that in passing to the colourless state radiant energy is visibly emitted. Perhaps a word of explanation is advisable on the question of the production of the coloured state by the absorption of light energy by the colourless state. It must be remembered that although the colourless state is markedly transparent to the short wave ultra-violet light, it possesses a definite and measurable absorptive power towards that light. Since it is this light only which effects the change it may be accepted without hesitation that the change is due to the fraction of that light which is absorbed.

Then again, reference may be made to some investigations carried out in Liverpool which also support the existence of two states of different energy content, the change from the higher to the lower

[1] See p. 101

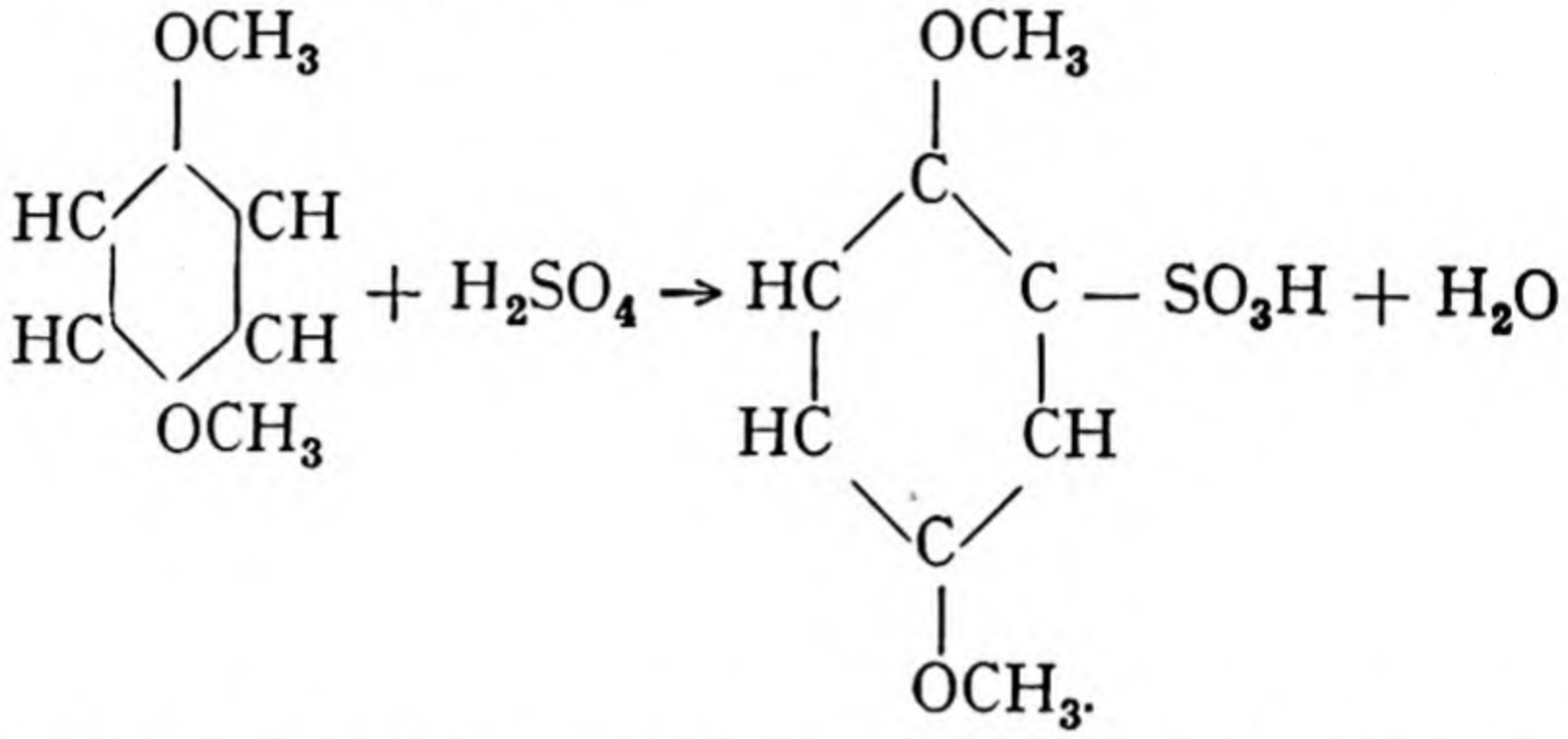
being associated with fluorescence and phosphorescence. Inasmuch as these observations concern absorption spectra to a certain extent they will be more fully discussed in Vol. IV., but they may be mentioned here so far as they are connected with fluorescence. It has long been known that many organic compounds exhibit entirely different absorption spectra when dissolved in different solvents. A very characteristic instance of this phenomenon is given by the ethyl and methyl ethers of phenol, hydroquinone, resorcinol, etc., since the solution of each in alcohol is colourless and exhibits an absorption band in the ultra-violet, whilst their solutions in concentrated sulphuric acid are red and selectively absorb light of much longer wave-length. In order to obviate a possible criticism it may be stated that the ethers are not chemically changed by dissolution in concentrated sulphuric acid, since they may be recovered unchanged by pouring the acid solution on to crushed ice. Clearly, however, some physical change is induced by the change in solvent as the absorptive powers of the two solutions of each phenolic ether are very different.[1]

Now these phenolic ethers in alcoholic solution are fluorescent, the luminescence being caused by the absorption of light of wave-lengths lying within the absorption band of which mention has already been made. This has been proved by the use of a monochromator, when it was found that the whole fluorescence band was emitted when monochromatic light of any wave-length within the absorption band entered the solution. When the fluorescence band of these ethers is measured it is seen to extend over the same wave-lengths as are absorbed by the ethers when in solution in concentrated sulphuric acid. In other words, the same smaller frequencies are characteristic of each substance, but in the one case (alcoholic solution) they are evidenced as fluorescence emission, and in the other case (sulphuric acid solution) they are evidenced as an absorption band. As is frequently the case with organic components in solution, neither the absorption bands nor the fluorescence bands have as yet been resolved into their compounds, and consequently it cannot be stated that the individual components of the fluorescence bands are identical with those of the absorption bands of the sulphuric acid solutions. In view of the fact that both bands lie in the same spectral region, it may, however, be accepted that they are similar.

The next question which arises is whether there is any evidence that we have two different states of the same phenolic ether molecule when in solution in the two solvents, and that the energy content of the molecule in sulphuric acid solution is greater than that of the molecule in alcoholic solution. These two points may be discussed separately, for the arguments are different. In the first place, the existence of the molecules in two different physical states is clearly demonstrated by the different properties which they exhibit when in

[1] Baly and Rice, *Trans. Chem. Soc.*, **101**, 1475 (1912).

solution in the two solvents. It might be considered that the fact that the absorption spectra of the molecules in solution in the two solvents are entirely different is sufficient to prove this, but there is also to be added to this the fact that the chemical properties are different in the two states. A very characteristic chemical reaction of aromatic compounds, such as the phenolic ethers, is that with sulphuric acid, whereby they are converted into their sulphonic acids. This may be exemplified by the formation of the sulphonic acid of hydroquinone dimethylether :—



Although only one molecule of sulphuric acid is necessary to convert one molecule of the hydroquinone ether into the sulphonic acid, yet the addition of an excess of the acid to the alcoholic solution does not cause the reaction to take place even on warming. On the other hand, when the ether is dissolved in concentrated sulphuric acid and exhibits a different absorptive power, sulphonation takes place readily enough on gently warming. The progress of the reaction can be followed with the spectroscope, since the absorption spectrum changes to that characteristic of the sulphonic acid. The evidence would seem to be very definitely in favour of the existence of two different states of the same molecules in the two solvents and the characterisation of these two states by different physical properties (absorption spectra) and by different chemical properties.

Although the chemistry of the whole problem will be discussed in detail when we come to the subject of absorption spectra in Vol. IV., yet it may be stated here that the modern view of chemical reaction falls into line in a very remarkable way with the above conclusion. Briefly expressed, this theory states that molecules in their normal states do not undergo reaction, and that it is first necessary to convert them into an active state, a change which is accomplished by the supply of energy to them. The amount of energy required to change a single molecule from the normal non-reactive state to the activated and reactive state is called the critical increment of energy of that molecule, it being unnecessary to assume that this critical increment is the same for all the reactions which a given molecule can undergo. It will be seen that the fundamental basis of this theory is the existence of at any rate two states of the same molecule having different energy contents, the reactive state having the greater energy content.

In general, particularly with gaseous reactions, the formation of the active state during the course of the reaction cannot be demonstrated, the velocity of the reaction of the activated molecules being too great. On the other hand, the necessity for the supply of the critical increment of energy to the non-reactive molecules has been definitely proved.

It would seem, however, that in the case of the phenolic ethers described above we have obtained concrete and visible evidence of the existence of the activated state, namely, the state which exists in strong sulphuric acid solution, for there can be no doubt that this state is not only an intermediate one in the sulphonation reaction and that it is this state which undergoes that reaction. On the other hand, this particular set of observations gives us no evidence that the activated intermediate state has a greater energy content than the non-reactive state in which the molecules of these compounds exist when in alcoholic solution. We find ourselves in a very interesting position. On the one side we have the accumulated evidence of physical chemists that molecules must be converted into an activated state by the supply of a definite amount of energy for them to enter into a reaction, the activated state not having been identified. On the other side we have the spectroscopic evidence of the existence of the activated state, the greater energy content of that state not having as yet been proved. It is difficult to believe that these two sets of observations do not harmonise and that the latter does not complete the former. We are led to believe that the activated state of the phenolic ethers in sulphuric acid solution is a state of greater energy content than that which exists in alcoholic solution, and that the difference of energy content between those two states is the critical increment of the sulphonation reaction.

So far as the spectroscopic evidence has been able to help us, all that we know is that the phenolic ethers exist in two different states when in solution in our two solvents, and that the reactive state exhibits an absorption band situated nearer to the red than does the inactive state. Up to the present we have no information as to the relative energy contents of the two states or, indeed, as to whether there is any difference of energy content between them at all. As a matter of fact there is ample evidence to be gained from absorption spectra as to the reality of the energy difference and indeed in the sense required to harmonise the spectroscopic and chemical observations.

The essential fact that we have to prove in order to achieve this is that in the case of two different physical states of the same molecule, the state which is characterised by the absorption band of longer wave-length has the greater energy content. It must be understood once and for all that our experience as to the existence of two or more different states or phases of molecules is entirely based on evidence gained from absorption bands in the visible and ultra-violet regions. Within that experience the proof we require as to the greater energy

content associated with the phase which absorbs the longer wave-lengths is perfectly definite and quite general.

There is no need to anticipate the whole story to be told later under absorption spectra, and it will be sufficient to describe three observations.

In the first place, reference may again be made to the two physical states of fused quartz, namely, the colourless normal phase with its absorption band in the extreme ultra-violet, and the coloured metastable phase, with its absorption band within the visible region, this latter being produced by the supply of energy to the former.

In the second place, it is well known that many substances, such as pyridine, piperidine, benzaldehyde, etc., show different absorption spectra in the liquid and the vapour states. In these cases the supply of energy necessary to produce the vapour from the liquid causes a marked shift of the absorption towards the longer wave-lengths. For example, liquid piperidine is transparent to the long wave ultra-violet, whereas the vapour shows an absorption band in that region. Again, the absorption band of liquid pyridine has its maximum at $1/\lambda = 3876$, whilst the absorption band of the vapour has its maximum at $1/\lambda = 3587$.

In these cases we have evidence that the molecules exist in two different phases in the two physical states of gas and liquid and once again we find that the phase with its absorption band nearer the red has the greater energy content.

As the third piece of evidence we may take the case of trinitrobenzene, which gives a colourless solution in alcohol and a red solution in piperidine. Each solution has a characteristic absorption band, that of the piperidine solution being nearer to the red and indeed in the visible region, whilst in the case of the alcoholic solution the band is situated in the ultra-violet. Here we find again the existence of two different states of the trinitrobenzene molecule and the phenomenon is quite analogous to that observed with the phenolic ethers. That the red coloured phase of trinitrobenzene has the greater energy content can be readily proved in the following way. If there be added to the colourless alcoholic solution a small quantity of piperidine, say one molecule to every ten molecules of the nitro-compound, no change is produced in the absorption spectrum. If now this solution is exposed to ultra-violet light it slowly develops a red colour and the solution then exhibits the absorption band characteristic of the solution in pure piperidine. Obviously therefore some of the trinitrobenzene is converted by the action of the light into the red phase, and hence the phase must have a greater energy content than the colourless phase. If this red solution is now placed in the dark, the red colour and the relevant absorption band slowly disappear, the final condition being that the absorption spectrum is the same as that of the alcoholic solution. The change of colour on exposure to light and its disappearance in the dark may be effected as many times as desired. This disposes of the possibility that the colour change is due to a photochemical transformation of the tri-

nitrobenzene in the ordinarily accepted sense, that is to say, into a different chemical compound.

Although there exists more evidence in support of the present argument, evidence which will be given in Vol. IV., the above three observations are sufficient to justify the conclusion that when a molecule is changed from one state or phase to another, and when this change is accompanied by a jump in the position of the absorption band in the visible or ultra-violet regions towards the longer wave-lengths, the change is associated with an increase in the energy content of that molecule.

Now this conclusion does not conform to the generally accepted view as regards the characteristic vibration frequencies of molecules. In the theory of band spectra, which has as its fundamental basis the rotation-vibration frequencies of the molecules, it is held that the converse is true, the view being that when a molecule is thrown by the supply of energy into a new vibrational state the resulting system of rotation-vibration frequencies is shifted towards the shorter wave-lengths. This divergence must not in any way be interpreted as being antagonistic to the rotation-vibration theory, nor must it be concluded that the undoubted validity of this theory undermines any confidence that may be placed in the evidence that is now brought forward. Rather must we conclude that there exists two different mechanisms whereby radiation and absorption of energy can take place in the visible and ultra-violet regions. That such is the case does not only impress itself on our minds on account of the present evidence, but it is also very noteworthy that when molecules, under the influence of electrical excitation, emit a band spectrum in these regions, the structure of that spectrum is of the type explained by the rotation-vibration theory and is different in many respects from the structure of phosphorescence, fluorescence, and absorption bands. It is very probable that these two mechanisms are not unrelated to one another, since recent work seems to show that the rotation-vibration theory forms an integral part of the complete theory of absorption. All we can say at present is that, so far as fluorescence, phosphorescence, and absorption spectra in the visible and ultra-violet regions are concerned, the rotation-vibration theory is incomplete and insufficient to explain the whole of the observed phenomena.

When the arguments now brought forward in favour of the existence of molecules in different phases of different energy contents, each characterised by a different system of frequencies, are applied to the phenomena of fluorescence and phosphorescence, it is somewhat remarkable how readily these luminescence phenomena find a simple explanation. In making use of these arguments the first question which comes to our notice is the quantities of energy which are involved, since up to the present we have only dealt with the energy relationships in a qualitative sense. If the energy quantum theory be applied, it follows that, when a single molecule absorbs or radiates energy at a frequency characteristic of the phase in which it happens

to exist, each radiation or absorption process is associated with a quantum of energy defined by the product of the oscillation frequency into the universal constant, $h = 6{\cdot}5 \times 10^{-27}$, and if ν be the frequency the energy quantum is $h\nu$ ergs. In connection with this a very interesting and important investigation has been carried out by Schmieder [1] on the quantitative relations between absorption and luminescence. It is not possible to describe in detail the experimental methods employed by him, which are based on Lenard's work on the economy coefficient of luminescence, that is to say, the ratio of the emitted energy to the energy of the light absorbed in exciting that emission. Three phosphorescence bands were used, CaBiα, ZnCuα, and CaCuα, and for exciting them the mercury rays $\lambda = 435\mu\mu$ and $365\mu\mu$ were employed singly, making six measurements in all. Schmieder's results are of great importance, since he proved that for every energy quantum of exciting light absorbed, one energy quantum of luminescence is emitted. In general the exciting quantum of energy is larger than the emitted quantum, since the frequency of the former is the larger (Stokes' rule), and Schmieder further proved that the excess of energy, that is the difference between the two quanta, appears as thermal radiation, *i.e.* radiation in the infra-red. The first of these results is not new, because Lenard had convinced himself of its truth in 1914.[2] Schmieder's results can be algebraically expressed by the equation

$$h\nu_1 = h\nu_2 + x$$

where ν_1 is the exciting frequency, ν_2 represents the frequency of the resulting luminescence, and x is the energy radiated in the infra-red.

The experimental results described previously suggest at once an explanation of the phenomena of phosphorescence and fluorescence, which is in full accord with Schmieder's measurements. It may be assumed that the molecules of the phosphore, previous to activation, exist in a phase or an equilibrium of phases which is stable under the conditions of their environment. When these molecules are exposed to radiation of a frequency characteristic of their normal state, energy is absorbed and the molecules are converted, partly or wholly, into a phase of greater energy content, this phase being characterised by frequencies which are situated nearer to the red. This energised condition is either entirely unstable or metastable, and the activated molecules return to their normal state either instantaneously or slowly, this return process being accompanied by that radiation of energy which we recognise as luminescence. The oscillation frequencies of this luminescence are characteristic of the unstable or metastable phase of greater energy content.

Granting that this assumption is justified by the experimental observations previously adduced, the application of the above algebraical expression of Schmieder's results leads to most interesting

[1] *Ann der Phys.*, **77**, 381 (1925). [2] *Heidelberger Akad.*, 1914, p. 63.

results. In the first place, we have for every exciting quantum of energy absorbed, $h\nu_1$, the evolution of one quantum of luminescence energy radiated, $h\nu_2$, which is characteristic of the phase of greater energy content. It follows at once, therefore, that the difference in energy content between the normal and energised phases is equal to x ergs. The amount of energy necessary to cause the change in phase, that is the critical increment of energy, is thus equal to x ergs per molecule.

In the second place, we can sub-divide the whole process into two stages, namely, activation and de-activation. In the first stage each molecule absorbs one quantum $h\nu_1$ and is thereby converted into the phase of higher energy content. In the second stage the latter phase reverts to the normal phase, with the radiation of energy. The recognition of these two stages leads to the conclusion that there are two different possibilities as regards the radiation of the energy, and that fluorescence and phosphorescence are separate and distinct phenomena, not to be confused with one another. This conclusion can be demonstrated in a simple way if we generalise the algebraical expression of Schmieder's measurements, and base this generalisation on the fact that he did not associate the evolution of the quantity x ergs in the infra-red with either the energising or de-energising stage of the complete process. We may write the algebraical expression in the general form :—

$$h\nu_1 = \mathrm{A} + \mathrm{B},$$

where B is the difference between the energy contents of the two molecular phases involved in the process. There are then three alternatives, according to whether A or B or neither A nor B is equal to $h\nu_2$. These three alternatives may be considered in turn.

1. $\mathrm{A} = h\nu_2$. In this case the original absorption of a single quantum of energy $h\nu_1$ produces a phase change in the molecule, of which the energy increment is equal to B ergs. The excess energy is radiated as one quantum of $h\nu_2$ ergs at the frequency characteristic of the unstable phase, the radiation taking place during the activation process. The reverse process on the change of the molecule back to its normal phase is associated with the evolution of B ergs in the infra-red. Since in this case the luminescence emission takes place during the activation process, it cannot persist after the exciting light is removed. The name fluorescence may be applied to this case.

2. $\mathrm{B} = h\nu_2$. In this case the original absorption of the single quantum of energy $h\nu_1$ produces a phase change in the molecule, of which the energy increment is $h\nu_2$ ergs. The excess energy of A ergs is radiated in the infra-red during activation. The luminescence quantum of $h\nu_2$ ergs is radiated during the reverse process or the return of the activated molecule to its normal state. Since in this case the luminescence quantum is radiated during the de-activation process, we have here the possibility of the luminescence persisting after the exciting light has been removed, the period of persistence

depending on the slowness of the restoration process of the activated molecules. We may define this case as phosphorescence.

3. A $\mp h\nu_2$ and B$\neq h\nu_2$. In this case the whole of the absorbed quantum of $h\nu_1$ ergs is radiated in the infra-red and there is no fluorescence or phosphorescence in the ordinary sense. This is the condition which most usually obtains when substances absorb light energy.

Although the theory we are discussing is not able to define the conditions which determine the occurrence of any one of the above three cases, we may gain one further piece of information as regards the first two alternatives. It is quite evident that, provided that the right conditions obtain, there is no restriction in case I as to the relative sizes of $h\nu_1$ and $h\nu_2$. The absorption band and the fluorescence band may be situated close together in the spectrum, as indeed is commonly the case in true fluorescence phenomena. On the other hand, in the second case, namely phosphorescence, we have the condition that the difference in energy content of normal and activated phases is equal to one quantum radiated by the activated phase. Since the quanta are proportional to the frequencies characteristic of the two phases, it is obvious that there must be a lower limit to the difference between the frequencies of the absorption and phosphorescence bands, in order that the difference in energy contents may be sufficiently large to appear as one quantum in the visible region when radiated. It follows that in cases of true phosphorescence the absorption and luminescence bands cannot be situated very close together, there being a lower limit to the frequency difference between them.

This conclusion would seem to be borne out by experimental facts, as has already been pointed out in this chapter. We have, for instance, the fluorescence of the uranyl salts excited by light, with the absorption band and luminescence band situated close together and indeed overlapping to a certain extent. On the other hand, the uranyl salts are excited by cathode rays at — 185°, the luminescence spectrum being identical with that given under photo-excitation at the same temperature. Although it is not possible in the case of cathode ray excitation to specify the size of the activating quanta of energy, it is certain that the activation takes place under conditions which correspond with photo-excitation at much smaller wave-lengths than that of the light absorption band. In other words, the difference between exciting and luminescence wave-lengths is much greater than in the case of the fluorescence.

The same phenomenon has been observed with many organic compounds which fluoresce at ordinary temperatures under photo-excitation. As has been shown by von Kowalski and by Goldstein these compounds exhibit true phosphorescence when excited at — 185° by light or by cathode rays. The phosphorescence emission takes place at longer wave-lengths than does the fluorescence emission, and indeed the cathodo-phosphorescence has a longer wave-length than the photo-phosphorescence. This was instanced in Table LXVI. on p. 322.

There is one question which at once arises from our hypothesis in particular reference to the physical differentiation between fluorescence and phosphorescence. As was explained in the section dealing with the fluorescence of the uranyl salts, Nichols and his colleagues proved that this fluorescence has a definite rate of decay. It is true that this is very rapid, but there is undoubtedly a period of " persistence " which has been measured. It was at first believed that this decay of fluorescence is different in type from all other decay rates observed with true phosphorescence, but it was subsequently shown that the same type is characteristic of the photo-luminescence of calcite, the cathodo-luminescence conforming to that of true phosphorescence.

It would be expected from a superficial outlook that fluorescence, if the present hypothesis be correct and the radiation be associated with the process of activation only, must cease absolutely instantaneously when the activation process is stopped. In short, the first criticism would be that the very fact of there being a finite period of decay must entirely negative the hypothesis now brought forward. Such a criticism would, however, be premature, since there is one factor which still remains unknown. There is no question but that the activating quantum of energy $h\nu_1$ is greater than the fluorescence quantum $h\nu_2$, and that the very first stage of the whole process must consist of the absorption by one molecule of $h\nu_1$ ergs. The second stage is the radiation of the fluorescence quantum $h\nu_2$ with the formation of the activated state of the molecule, the critical increment of which is the difference between the two quanta $h\nu_2 - h\nu_1$. We have no knowledge whatever of the life period of the molecule at the end of the first stage, that is to say when it has absorbed the quantum $h\nu_1$. If the life period is finite then it is evident that the fluorescence emission will have a finite persistence depending on the average life period.

In order to clarify our ideas the argument may be re-stated. The complete process of the fluorescence radiation by a single molecule consists of three stages :—

1. The absorption of the single large energy quantum $h\nu_1$ at the absorption frequency ν_1.

2. The radiation of the smaller quantum $h\nu_2$ at the fluorescence frequency ν_2 and the formation of the activated state, the critical increment of which is given by $h\nu_1 - h\nu_2$.

3. The return of the molecule from this activated state to its original and normal state, accompanied by the radiation of the critical increment $h\nu_1 - h\nu_2$. Since, in the cases of true fluorescence, the frequency interval between the absorption and fluorescence frequencies is small, this critical increment $h\nu_1 - h\nu_2$ is small and will be radiated in the infra-red, even if it is radiated at a single characteristic frequency.

The question which concerns us now is the life period of the molecule at the end of the first stage, when it has absorbed the quantum

$h\nu_1$. If this life period has a finite and measurable value, then the fluorescence observed will have a finite and measurable rate of decay when a large number of molecules are exposed to the activated light rays and absorb quanta of the size $h\nu_1$. If every molecule at the end of the first stage has a fixed and specific life period, then the fluorescence will persist for that period only after cessation of activation and will then suddenly vanish. If, as is more probable in the case of crystalline solids, there is an average value of this life period, there will then be observed a measurable rate of decay of fluorescence, analogous to that of phosphorescence with extremely short persistence. It does not follow, however, that the decay rate will be of the same type in the two cases, because in the case of true phosphorescence the decay rate depends on the stability of the activated system, this being determined by the composition of the phosphore and the temperature, whereas in the case of true fluorescence the decay rate depends on the life period of individual molecules which have gained an amount of energy which exceeds that characteristic of the activated state.

Again, if this average life period of the molecules at the end of the first stage exists, then the intensity of the fluorescence will have a rate of growth comparable with its rate of decay. Immediately after excitation begins fluorescence will make its appearance, since some of the energised molecules will at once enter the second stage, and the intensity will increase to a maximum when the number of energised molecules formed in unit time equals the number entering the second stage. As already pointed out on p. 313, the dark interval between the instant of commencing activation and the first appearance of fluorescence is extremely short, being about 2×10^{-7} seconds with barium platinocyanide crystals and 2×10^{-8} seconds with a solution of rhodamine. There still are required measurements of the rate of growth of the intensity of fluorescence, and on p. 312 I urged the importance of these measurements. It is necessary that they be made with the pure substance, such as a uranyl salt, where the rate of decay is known and there is no danger of self-activation or auto-absorption, since only one unit of associated frequencies functions in the fluorescence emission.

Brief reference may be made to certain other facts in connection with our subject of luminescence in order to make the story a little more complete. The first of these is the overlapping of the absorption band and luminescence band in cases of fluorescence, such as has already been noted with the uranyl salts. This overlapping of the two bands has been viewed as a contradiction of Stokes' rule, this being stated very definitely by Gudden.[1] This raises the whole question of the breadth and structure of these bands, for a real contradiction of Stokes' law is impossible on the energy quantum theory. If a substance absorbs an energy quantum at one single frequency

[1] *Phys. Zeitsch.*, **24**, 465 (1923).

and subsequently radiates this energy increment as one quantum at another frequency, this second frequency cannot be larger than the first, since if it were so the radiated energy would be greater than that absorbed, and we could construct therefrom an ideal refrigerating machine. It is this phenomenon only that would contradict Stokes' rule. The problem is, however, not as simple as this since we find in the cases of fluorescence and phosphorescence that there is not one single absorption frequency and one single luminescence frequency but a band of associated frequencies in each case, and in many instances of fluorescence the two bands overlap to a certain extent, that is to say, a portion of the short wave side of the fluorescence band is superposed on a portion of the long wave side of the absorption band. This overlapping has been studied in great detail by Nichols and his colleagues as has previously been noted.

As far as our present knowledge extends, all absorption and luminescence bands exhibited by molecules in the visible and ultra-violet regions possess a definite structure, which is apparently of the same type in each case. Many bands have not yet been resolved into their components, but wherever this resolution has been observed the same type is found to be present. The first stage is the resolution of the bands into sub-groups which are symmetrically distributed on each side of one sub-group of maximum intensity. Further analysis resolves each of these sub-groups into short series of lines, the frequencies of which can be expressed by a simple formula.[1] Each sub-group is thus complete in itself and all of them are similar to one another within a single band group. As already stated one sub-group exhibits a maximum intensity, those on each side of this central one having a progressively decreasing intensity. There is little doubt that these sub-groups are due in part to the combinations of the central frequency of maximum intensity with multiples of a second characteristic frequency, in that the central frequencies of all the sub-groups can be expressed by a formula of the type

$$\nu = \mathrm{F} \pm \mathrm{A}m,$$

where F is the central frequency with maximum intensity, A is the second characteristic frequency and $m = 0, 1, 2$, etc.

Since the central frequency of each sub-group is associated with a number of other frequencies, the structure of the complete band group can be expressed by

$$\nu = \mathrm{F} \pm \mathrm{A}m \pm \mathrm{X},$$

where X is a function of a series of integers.

When a band group is not interfered with by other band groups on either side of it, observation shows that it is symmetrical in structure and that there are the same number of sub-groups on either side of the central sub-group. There will be found therefore for each value of m

[1] There is evidence that in certain cases the structure is more complex still.

two sub-groups, the associated frequencies of which can be expressed by

$$\nu = F + Am \pm X$$

and

$$\nu = F - Am \pm X.$$

Now it was shown by Nichols and his colleagues in the case of the uranyl salts that the fluorescence can be excited by any individual frequency which is part of the absorption band group. I have also found the same to be true in the case of many fluorescent organic compounds. In both cases the whole of the fluorescent band group is emitted even though the substance is excited by one component line of the absorption band group. The phenomenon is therefore not a simple one, but in view of the fact that for every frequency greater than the central frequency F there is a corresponding one smaller than F, the mean of the two being equal to F, it cannot be argued that Stokes' rule is contradicted. Let us suppose that fluorescence is excited by the monochromatic radiation of frequency B, which lies on the extreme red side of the absorption band, this excitation giving rise to the radiation of the complete fluorescence band group. For every component frequency radiated which is greater than B there is the corresponding smaller frequency. Even though we may not know the complete mechanism of the radiation, the net result is that the sum of all the energy quanta radiated is equal to an integral number of energy quanta at the central frequency F.

As a second matter of interest we may consider the reversal of some of the components of the fluorescence band, that is to say their observation as absorption lines by Nichols. According to the theory which is now put forward the fluorescence frequencies are characteristic of a definite phase of the molecules which differs from the phase which normally absorbs the exciting energy. If that phase is actually present, then it follows that the frequencies characteristic of it will be capable of observation by absorption spectra methods, and hence the phenomenon of " reversal " is actually to be expected.

One of the most interesting advances made recently is that of the Tesla luminescence spectrum discovered by Professor Stewart and his colleagues.[1] The case of benzene is of peculiar importance in connection with the phenomenon of reversal. There are two characteristic spectra of benzene, namely, the absorption band group and the corresponding fluorescence band group, each having its own structure and each being observed separately. Under excitation by the Tesla discharge both appear as a fluorescence spectrum, the whole of the absorption band group now being completely reversed. On the present theory the two spectra, fluorescence and absorption, are due to two phases of the benzene molecule, each having its own characteristic frequencies. In the Tesla luminescence phenomenon both phases take part.

[1] See p. 283.

If we sum up the experimental observations which have been recorded in the field of fluorescence and phosphorescence it may be seen that the phenomena grouped under the general name of luminescence are much less common than the ordinary cases where radiant energy is absorbed and no measurable amount of luminescence is to be detected. In the latter cases the absorbed energy must radiate as thermal energy in the infra-red. It would seem to follow from what has already been advanced in favour of the phase hypothesis that the factor which determines whether luminescence occurs or not must be a function of the stability of the activated state, the formation and normalisation of which are the origin of the luminescence radiation. The word normalisation is here used to describe the loss of energy whereby the phase of higher energy content reverts to the phase existent under normal conditions in the dark.

We may now discuss in detail this question of the stability of the activated state since it would seem that in the change of stability may very possibly be found the explanation of many of the observed phenomena. In so doing we may take into consideration both fluorescence and phosphorescence, which, according to our hypothesis, are two different phenomena, the former being the radiation of the excess energy during activation, whilst the latter is the radiation of the difference of the energy content of the normal and active phases during normalisation. In both cases the visibly emitted energy is radiated at the frequencies characteristic of the activated phase. Since in the case of phosphorescence the difference between the energy content of the two phases of a molecule, activated and normal, is equal to the energy quantum characteristic of the activated phase, it follows that there must be a specific relation between the phases for phosphorescence to occur. If, as before, $h\nu_1$ is the activating quantum absorbed by the normal phase, and $h\nu_2$ is the quantum characteristic of the activated new phase, and if the difference in these two quanta is equal to $h\nu_2$, then

$$h\nu_1 - h\nu_2 = h\nu_2$$

and

$$h\nu_1 = 2h\nu_2.$$

Expressed in terms of the algebraic equation previously given the condition necessary for phosphorescence is that

$$A = B = h\nu_2.$$

This was implied on p. 340 in the condition given for phosphorescence to take place. All that this means is that phosphorescence can only occur when there is a simple integral relation between the frequencies of the normal, absorbing phase and the activated phase.[1]

An important result of this essential condition is that the fluorescence radiation is the same as the phosphorescence radiation and in

[1] It is possible that the general condition for phosphorescence is that the activating quantum may be any integral multiple of the quantum characteristic of the activated phase.

this we find an explanation of many observations made first by Lenard and Klatt and now familiar to all who have worked in this field.

If the activated state be considered quite generally, then three conditions can obtain in which the activated state has complete metastability, a finite stability, and total instability, respectively. Each of these may be separately discussed with respect to the luminescence phenomena which will occur when the normal phase absorbs energy at its characteristic frequency.

1. *Complete metastability of the activated state.*—When the energy is absorbed by the normal phase the activated phase is produced and, since the new condition is completely metastable, the energy increment of the system is retained for an indefinite period, until by some means or other the stability is decreased, when it will be radiated as phosphorescence. The excess energy over and above that required for the activation is radiated and, if this takes place as fluorescence, then, owing to the specific condition necessary for phosphorescence, this fluorescence will take place at the frequencies characteristic of the active phase, that is to say, the frequencies of the fluorescence will be identical with those of the latent phosphorescence of the activated system. In this case there will be seen during the excitation the emission of luminescence at those frequencies characteristic of the phosphorescence which can be released by such means as heat. This fluorescence band will disappear at once when the excitation is stopped, and we therefore find the instantaneous band of Lenard and Klatt, which is visible only during the storage of energy in the formation of the activated state.

Although this excess energy can be radiated as quanta at the frequencies of the activated phase, we cannot assume that it must be so radiated. It is possible that it may be radiated in the infra-red, in which case no luminescence of any sort will be seen during activation.[1] The absence of any luminescence during activation is frequently seen, as for example in the activation of fluor spar and the halogen salts of the alkali metals.

There is one important conclusion which may be drawn from our hypothesis, and this may be mentioned here, although it is true for all conditions in which the activated phase has a definite life period. The increment of energy stored up in activation is specifically characteristic of a particular phase change and consequently can only form the origin of a specific set of phosphorescence frequencies. This is in full accordance with Lenard and Klatt's statement that the energy stored up at one set of frequencies can only be utilised in the production of one phosphorescence band.

It is evident on the present hypothesis that with a limited quantity of substance there must be a limit to the amount of energy stored

[1] There is yet another possibility, namely, that owing to the integral relationship the excess energy of activation is re-absorbed by the system to form two (or more) activated molecules. There is at present not sufficient evidence to justify the inclusion of this as a definite alternative.

up, this limit being reached when the substance has been fully converted into the activated state. As this limit is approached the quantity of energy that is stored up in unit time will decrease and consequently the fluorescence emission will also decrease. Such a condition may conceivably be reached in the surface layer of a solid substance and it may be suggested that this is the origin of the "fatigue" effect that can be seen in the well-known Crookes cathode ray tubes. The most familiar example is that in which a solid object, *e.g.* a cross, is placed between the phosphore and the cathode, whereby within the shadow cast by the object no luminescence is visible. If now, after the discharge has been passed for some time, the cross is removed from the path of the electron stream, those parts of the phosphore which had previously been screened luminesce with a greater intensity than those parts which had previously been exposed to the cathode rays.

Again, the whole basis of our hypothesis is the existence of molecular phases of different energy content, each of these being characterised by its own set of co-ordinated frequencies which are evidenced either as a single absorption or luminescence band group. If a substance exhibits phosphorescence in the visible region, then the active phase of that substance will be able to absorb visible light of the same frequencies as the phosphorescence emission. When such a phosphore is activated, the activated state being completely metastable, it will exhibit a visible colour. To observe this colour it is obviously necessary that all phosphorescence emission must be absent. If the activated state is viewed by transmitted light, then the colour will be complementary to that of the phosphorescence emission. Thus the amethyst colour of activated silica glass is complementary to the green of its phosphorescence. If the substance is crystalline and is viewed by reflected light from its crystal faces, the colour will be the same as that of the phosphorescence, since maximum reflection takes place within the region of its absorption band. It is this latter colour relation that Lenard and Klatt say they observed with their activated solid phosphores.

2. *Activated state having a finite stability.*—In this case the activated state will begin to lose energy immediately after formation, with the result that the phosphorescence characteristic of the active phase will become visible. As more and more of the molecules become converted into the active phase the intensity of this phosphorescence will steadily increase up to a maximum value. If the activation be stopped at any moment, then at that moment will the activated state contain a definite increment of energy. The velocity at which this increment is radiated will be inversely proportional to the stability of the activated state; the greater the stability the longer will be the time taken in the return to the normal state and consequently the greater will be the persistence and the smaller will be the intensity of the phosphorescence. The persistence and intensity will be in inverse ratio to one another.

In this case, as in the first, the fluorescence energy will be radiated during excitation, either as visible luminescence at the phosphorescence frequencies or in the infra-red. In the former case there will be a sudden fall in the intensity, but no change in the wave-length of the luminescence, when the excitation is brought to an end. In the latter case when the fluorescence energy escapes at invisible frequencies, the phosphorescence only will be visible during excitation and the new phenomenon will be observed of a more or less rapid rise in the intensity of this phosphorescence to a maximum. There will therefore be no measurable change in intensity at the instant the excitation ceases. This also is in accordance with Lenard and Klatt's observations.

Within this condition of finite stability there must be included all grades of stability from very great to vanishingly small, and the variations in the luminescence phenomena associated with these grades follow naturally from what has already been said. It will be noted that as the stability decreases, the persistence of the phosphorescence will become shorter and the intensity greater. When the stability of the activated state is vanishingly small the persistence of the phosphorescence will be extremely short and its intensity will have a maximum value. It is of great interest to note that the greatest possible luminescence will be observed under a given intensity of excitation, when the excess energy is radiated as true fluorescence at the phosphorescence frequencies and the stability of the activated state is still finite but vanishingly small. 'It clearly must be a maximum since under these circumstances the whole of the activating energy is radiated during excitation, in part as fluorescence and in part as phosphorescence at the same frequencies, within a minute period after its absorption. It is also true that under any condition which falls within this class, the luminescence observed during excitation will always be greater than that observed when the activated state is completely metastable. This follows from the fact that in this second condition there will always be added a measurable amount of phosphorescence to that which evidences itself as fluorescence. In short, if it be possible progressively to decrease the stability of the activated state from complete metastability to the condition when it is still finite but vanishingly small, the total intensity of luminescence visible during excitation will progressively increase up to a maximum value. Lastly, under the final condition of vanishingly small stability the instantaneous disappearance of all luminescence will be observed when the excitation ceases.

3. *Activated state totally unstable.*—This condition is the same as that already defined on p. 340, namely, that in which neither A nor B is equal to $h\nu_2$. Under these conditions no luminescence of either kind, fluorescence or phosphorescence, is possible. The margin between this condition and that of the vanishingly small stability must be a very narrow one. In the progressive decrease of stability of the activated state, postulated above, a very small increase in the

disturbing influence, whatever this may be, will take the phosphore over the border line and cause all luminescence suddenly to vanish. The complete sequence of phenomena to be expected when the stability is progressively decreased, all other controlling factors being constant, will thus be a steady increase in the total luminescence up to a maximum, at which point the luminescence instantaneously vanishes when the excitation ceases, and this stage will almost immediately be followed by a sudden and total disappearance of all luminescence, however strong the excitation may be at the frequencies characteristic of the normal phase.

In discussing the factors which determine the stability of the activated state, it is not the stability of the active phase only that is concerned. At first sight it might appear that this were indeed the case, but a moment's consideration will show that the stability of the normal phase is equally concerned. The present hypothesis states that fluorescence and phosphorescence are manifestations which accompany the energy changes associated with the reversible change of one molecular phase to another, and, further, that with any specific fluorescence or phosphorescence band two specific phases of the molecule are concerned. It is obvious that if the activated molecular phase is rendered completely unstable the luminescence cannot occur, and it is equally obvious that the same must be true if the normal phase is rendered completely unstable, since if it does not exist it cannot absorb the activating energy, nor can an activated phase return to it by loss of energy. The problem of the stability of the activated state must therefore involve both that of the normal and that of the activated phases of the molecule.

If we turn once again to absorption spectra observations, these can give assistance in the study of the conditions which are normally present in the un-activated state. The major premise of our hypothesis is that an absorption band group is indicative of the presence of a specific molecular phase. When a transparent solid, such as a crystal or a solution of a compound, is examined, evidence is always found of the existence of more than one absorption band group.[1] This phenomenon when interpreted in terms of our hypothesis means that the molecules of any substance do not all exist in one single phase, but that there is always present an equilibrium between two or more phases, one of which is the phase we have called the normal phase, namely, the particular phase which absorbs the activating energy. If this equilibrium mixture is exposed to light of the frequencies characteristic of the normal phase the activated state will be produced, and the stability of that activated state must depend on the phase equilibrium. Any change in the phase equilibrium must either increase or decrease the stability of the activated state. It is a fact well established by experimental observation that the greatest stability of the activated state is found with pure crystalline substances. This is in accord with the experimentally proved fact that phosphorescence, *i.e.* finite

[1] The evidence in support of this statement will be given in Vol. IV.

stability of the activated state, is only observed with a substance disseminated through a diluent. If we start with a solid crystalline substance in which the activated state is completely metastable, and alter by some means the phase equilibrium, the stability of the active state will be decreased by an amount which depends on the extent to which the phase equilibrium has been shifted.

There are three factors which determine the phase equilibrium and these are :—

(*a*) Concentration in a solvent.
(*b*) Nature of the solvent.
(*c*) Temperature.

Each of these may be considered separately.

(*a*) *Concentration in a solvent.*—One of the earliest laws of absorption is that known by the name of Beer's law, which states that the absorptive power of molecules in solution is independent of the concentration. The formal expression of this law is given by

$$\log \frac{I_0}{I} \times \frac{1}{dc} = \text{constant},$$

where I_0 is the intensity of the incident beam of monochromatic light, I is the intensity of the same light after transmission through a layer of absorbing solution of thickness d and concentration c, the solvent being considered as having no absorptive power. Numerous experimental measurements have shown that within the region of an absorption band in the visible or ultra-violet this law does not hold, the absorptive power increasing with decrease in concentration. If the absorptive power of a crystal of known thickness and density be measured and then, successively, the absorptive power of solutions of the same substance with different concentrations, it is found that the absorptive power $\left(\log \frac{I_0}{I} \times 1/dc\right)$ increases with dilution from the minimum value given by the solid to a maximum. From some quantitative measurements of the absorptive power of pyridine in various solvents it would seem that the relation between the maximum absorptive power K exerted in a given solvent and the absorptive power k exerted at the concentration c in that solvent is given by

$$\frac{k}{K} = 1 - e^{-\frac{a}{c}}$$

where a is a constant characteristic of the solvent. It is true that statements have been made that Beer's law holds with one or two compounds, *e.g.* the metallic nitrates. It is, however, more than questionable whether this is the case for the complete range of concentration from the crystalline solid to dilute solutions. At any rate it is unquestionable that the vast majority of substances do not obey Beer's law and that the law is always disobeyed in the same sense.

It is thus evident that change in concentration alters the equilibrium between the phases. If we start with a pure crystalline sub-

stance in which the activated state is completely metastable and then form a solid solution of the substance in some inactive diluent, the stability of the activated state will be diminished by an amount which depends on the dilution in that diluent. If we consider this from the point of view of the luminescence of preparations containing different concentrations of the substance, the stability of the activated state will progressively decrease with the concentration. The result will be that as the concentration is decreased phosphorescence will make its appearance and the intensity will increase and the persistence will decrease. Further, the total luminescence observed during activation will increase, and, since the influence of the solvent or diluent increases to a maximum as the concentration is decreased, it is possible that we can find in this an explanation of the fact that as the dilution is increased the intensity of the phosphorescence rises to a maximum and then begins to decrease. In view of the fact that the influence of the solvent is limited, a stage of dilution must eventually be reached when the intensity falls owing to the smallness of the amount of active material present.

(*b*) *The nature of the solvent.*—The nature of the solvent or diluent can affect the phase equilibrium in two ways. In many cases a change in solvent appears merely to modify to a greater or less degree the equilibrium between the phases, the same phases being present in the equilibrium. In this case all that will be observed is a difference in the stabilities of the activated state obtained from solid solutions of the same concentrations in different solvents. This will be indicated by differences in the persistence and intensity of the phosphorescence bands given by equal excitation of phosphores with the same concentration in different fluxes. So far as I am aware there is no definite experimental evidence for or against this conclusion.

In some cases a change in solvent establishes an entirely new equilibrium, of which different phases form components. The same rules will apply to the effect of dilution on each such equilibrium, but the change of solvent will give rise to different phosphorescence and fluorescence emission. This would appear to have been observed by Lenard and Klatt, since with certain of their phosphores the luminescence bands observed depend on the particular flux used.

(*c*) *Temperature.*—In view of the fact that change of temperature alters the total energy content of a substance it would seem to be an obvious assumption that a change in the phase equilibrium is thereby caused. Apart from this, evidence from absorption spectra has already been adduced which shows clearly that marked changes are produced by changing the temperature. The cases quoted indicate a definite phase change which takes place when certain liquids are converted into vapour at their boiling-point and in certain other cases it has been found that the latent heat of evaporation at the boiling-point can be expressed in terms of the difference between the energy contents of two different molecular phases.[1] There is, further, evidence from

[1] Baly, *Phil. Mag.*, **40**, 30 (1920).

chemical reaction and from refractivity measurements which indicate very clearly that the phase equilibrium is a function of the temperature.

The effect of temperature in changing the phase equilibrium and hence in changing the stability differs in one respect from that of a solvent or diluent. In the latter case the effect increases up to a maximum with decreasing concentration, whilst in the former there is no reason to presuppose any such limit. For this reason there is every reason to expect that, starting with the condition of complete metastability of the activated state at a given temperature, a progressive rise of temperature will progressively decrease the stability until it becomes completely unstable. Moreover, the influence of temperature is the only one of the three which we can use to trace the whole sequence of phenomena observed when the stability of the activated state of a phosphore is reduced from that of complete metastability to zero. The phenomena to be expected from the present hypothesis have already been detailed, and the experimental verification of these may now be discussed. In order to do this we may conceive of a phosphore under constant excitation by light of the frequencies characteristic of its normal molecular phase and, further, we may so adjust the temperature that the activated state is completely metastable. If fluorescence emission occurs it will occur at the frequencies characteristic of the active phase and will vanish instantly the excitation is stopped. The luminescence band will thus be instantaneous in the sense defined by Lenard and Klatt. On raising the temperature a condition will soon be reached when the activated state assumes a finite stability and at that stage phosphorescence will begin at the same frequencies. When the exciting light is stopped there will be a sudden fall in intensity, not to zero but to a small value due to the phosphorescence, there being no change in wavelength. As the temperature is still further raised the intensity of the phosphorescence emission will increase and its persistence decrease. Further rise in temperature will bring the phosphore into the condition that the activated state has only a vanishingly small stability, when the total luminescence, phosphorescence, and fluorescence will cease the instant the exciting light is cut off. Once again we have the instantaneous band of Lenard and Klatt. In short, we find that two temperature regions exist where the phenomenon of instantaneous bands is observed, and these are separated by a third temperature region in which bands with measurable persistence are observed. This is in exact agreement with Lenard and Klatt's observations. Under the alternative condition that the fluorescence energy is radiated in the infra-red, the only difference in the observed phenomena will be, first, that in the lower instantaneous state storage of energy will take place without visible luminescence, and, second, that in the intermediate " persistence " state there will be no fall of intensity when the exciting light is quenched and consequently it will be possible to observe the growth of the phosphorescence intensity to a maximum value. The upper instantaneous state will not be

affected except that the intensity during excitation will be smaller than if visible fluorescence were present.

Quite a small increase in temperature will be sufficient to bring the phosphore from the condition of vanishingly small stability of the activated state to the condition when it is totally unstable. The temperature limits of the upper instantaneous state will therefore be small, and this was observed by Lenard and Klatt. It is obvious that the estimated lower limit of this state depends on the accuracy of the measurement of persistence and therefore cannot be clearly defined. It is sufficient for our purpose to show that such an upper instantaneous state must exist on our theory over a small temperature range and that the observed phenomena are in complete accord. The existence of a condition of complete instability of the activated state, which can be reached by rise in temperature, when no luminescence takes place, at once fixes an upper temperature limit to all fluorescence and phosphorescence phenomena characteristic of our activated and normal states. The existence of this upper temperature limit was confirmed by Lenard and Klatt and is familiar to every one who has worked in this field.

The whole of the foregoing argument as to the stability of the activated state refers to two phases only, the normal phase which absorbs the exciting energy and the activated phase thereby produced. The hypothesis gives us no information, so far as at present can be seen, regarding the possibility of the formation of an activated state with measurable stability by absorption of energy at a frequency which is different from that of the so-called normal phase. That such activation can occur above the upper temperature limit of the ordinary luminescence phenomena, such as Lenard and Klatt dealt with, is suggested by Nichols and Wilber's discovery of the phenomenon of flame luminescence. As indicated on p. 323 this phenomenon occurs at temperatures which in general are higher than the normal luminescence limit of the compounds they examined. It is evident that the excitation of the flame luminescence is caused by energy with different frequencies from those which stimulate the normal luminescence phenomena. This follows from the two observations recorded by Nichols and Wilber, first that the hydrogen flame alone has the power of stimulating this special luminescence, and second that the radiation from the mercury arc which stimulates the ordinary luminescence does not stimulate this particular type.

Returning once again to the effect of temperature, we have only considered the phenomena which evidence themselves at definite resting places on a rising scale of temperature. Mention may also be made of the phenomena to be expected when the temperature is suddenly raised to a higher value. Clearly the energy content at the lower temperature is greater than that normally present at the higher temperature under the same conditions of excitation. We would expect, therefore, that the sudden rise of temperature would cause a phosphorescence to manifest itself of considerably greater

intensity than normally would be visible under excitation at the higher temperature. This enhancement of the intensity will be the greater, the higher the temperature to which the activated phosphore is raised, the maximum intensity being obtained if the phosphore is heated to above the upper temperature limit of luminescence. Once again this seems to be in accord with observation. It is well known that the discharge of phosphorescence can be effected by exposure to infra-red rays as well as by raising the temperature, the infra-red rays producing the result without any measurable increase in the temperature of the phosphore.[1] This result is just that to be expected since the phenomenon is due to the disturbance of the normal phase equilibrium caused by an increase in energy content. This may equally well be supplied by raising the temperature or by absorption of infra-red radiation.

So far the effect of the three factors which disturb the normal phase equilibrium, namely, concentration, nature of solvent or diluent, and temperature, have been considered separately. It is of course possible for two of them, especially concentration and temperature, to be varied simultaneously. There is no need to discuss in detail the effect of such variation, but one particular result may be mentioned. As already explained, the maximum luminescence possible is given by a phosphore when the stability of the active phase is reduced to as small a value as possible. At room temperature this condition of stability will be obtained at a definite concentration of the active substance in the phosphore and, as has already been stated, this concentration is very small. Since both rise of temperature and decrease in concentration tend to decrease the stability of the activated state it follows that in order to obtain the maximum intensity of luminescence at a higher temperature a greater concentration is required. For every temperature there will be a corresponding concentration which will give the optimum of luminescence and the concentration required at, say 500° will be greater than that required at room temperature. There is little doubt that the luminescence of the incandescent gas mantle is due to the fluorescence and phosphorescence of the cerium oxide in solid solution in thorium oxide, and in this case the temperature is more or less fixed by the coal gas flame. It is of some interest to note that the concentration of cerium oxide required to give optimum luminescence of the gas mantle is greater than that required at ordinary temperatures, being about 1·0 per cent. It cannot be said that this fact has been entirely explained, since we are ignorant of the frequencies of the activating energy and the whole of our argument as to the effects of concentration, nature of solvent or diluent, and temperature are based on a constant condition of excitation at the same frequencies. It is justifiable, however, to point out that the facts observed are in accordance with those which the theory leads us to expect under constant conditions of excitation.

It may also be pointed out that certain other observations re-

[1] Wiedemann and Schmidt, *Ann. der Phys.*, **56**, 201 (1895).

corded by Lenard and Klatt may be explained by the combined effect of concentration and temperature. In the account given of their work it was stated that one and the same active principle in a phosphore gives rise to several luminescence bands, which are completely characteristic of that active principle. With a given phosphore these bands differ as to the temperature limits, that is to say, some appear at low temperatures and vanish at higher temperatures, whilst others appear only at higher temperatures and their upper temperature limit is considerably higher than in the case of the former. Their wave-lengths are not changed in any way by temperature so far as could be observed. It is evident that in such phosphores more than one active phase is produced, each having its own normal phase at which activation takes place. The activated state, therefore, can be a more complex condition than we have envisaged in the foregoing. The activated state as a whole, produced by illumination with light from $\lambda = 3900$ to $\lambda = 2000$ as employed by Lenard and Klatt, is a sum of a number of activated states, each with its own stability defined by temperature and concentration. If it be assumed, as seems quite reasonable, that the stability of all these activated states is not the same for the same values of concentration and temperature, then it will be found that with a given phosphore, having a definite concentration, different temperature limits will exist for the different bands, as Lenard and Klatt found.

It would also seem to follow from general principles that the stability of the activated states involving bands of longest wave-length, *i.e.* with the greatest energy content, would be the least and would have the lowest upper temperature limit. This indeed seems to be the case, since in those cases where more than one band is visible increase of temperature tends to shift the luminescence maximum towards the shorter wave-lengths, this having been proved by Nichols to be due to the relative increase in the intensity of the band of shorter wave-length.

In concluding this section I would point out, that, although the hypothesis of molecular phases meets with some success in the explanation of the phenomena of fluorescence and phosphorescence, there remain many observations which it is unable to explain. It has already been stated, for example, that the rate of decay of phosphorescence consists of two or three separate processes. If the time intervals measured from the instant of quenching the excitation be plotted against the reciprocal of the square root of the intensity of the phosphorescence emission, the decay during each separate process is expressed by a straight line, and these lines become progressively more inclined towards the time axis. In other words, the relation between rate of decay and time is different in each process, and each succeeding process has a slower rate. The explanation of this phenomenon is not forthcoming from our hypothesis. Whilst fully recognising its present limitations I have ventured to bring this hypothesis forward, encouraged by the hope that it may prove of use in the interpretation of the phenomena in this most attractive field.

CHAPTER V.

THE PHOTOGRAPHY OF THE SPECTRUM.

No attention has as yet been paid to the actual methods of photography employed in spectroscopy, and a few pages may well be devoted to this subject. It is familiar to everyone that the ordinary commercial photographic plate is sensitive to the blue region of the spectrum and also to part of the ultra-violet, and consequently such a plate may be used in photographing those regions of the spectrum. The main question which concerns us is the limit of practical sensitivity of the various photographic plates of commerce, and the methods which can be employed in order to be able to photograph regions of the spectrum which lie outside those limits. It is not possible here to discuss *in more historico* the developments that have taken place in photographic technique, but rather must we confine ourselves to those particular advances which are of especial value to the spectroscopist.

I take this opportunity of expressing my most cordial thanks to Dr. C. E. Kenneth Mees of the Eastman Kodak Company, Rochester, N.Y., for his great kindness in supplying me with much valuable information which he has allowed me to use in this chapter. This particularly refers to the methods of sensitising plates for photographing the red and infra-red regions. This section was written by Dr. Mees.

It is generally agreed as the result of measurements made by several observers that the maximum sensitivity of a normal photographic emulsion, containing silver bromide or mixtures of silver bromide and iodide, lies at or near $\lambda = 4500$. This is indicated clearly enough by the investigations of Leimbach [1] and of Luckiesh, Holladay, and Taylor.[2] On the red side of this maximum the sensitivity falls off rather rapidly to a small value near $\lambda = 5200$, this being due to the decrease in the absorptive power and hence in the photochemical activity of the silver halide with increase in wave-length. On the short wave-length side the sensitivity falls off more slowly to about $\lambda = 2400$, after which it decreases with considerable rapidity. This second and more rapid decrease is due to the absorptive power of the gelatine, which protects the silver halide from the direct action

[1] *Zeitsch. wiss. Phot.*, **7**, 157 (1909).
[2] *Journ. Franklin Inst.*, **196**, 353 (1923).

of the light. It follows from this that the ordinary photographic plate of commerce is quite satisfactory for use in spectroscopy within the limits of $\lambda = 5000$ and $\lambda = 2400$.

In general it may be said that two conditions should be aimed at in spectrum photography in order to obtain the best definition possible, namely, fineness of grain in the emulsion and strong contrast. The former is determined by the method of manufacture and the second by the method of development. I find that opinions differ amongst spectroscopists as to the best type of plate to use and the most satisfactory developer, but from experience of both emission and absorption spectra where the finest detail possible is a necessity, I confess to a strong predilection in favour of a good process plate, such as the Ilford, and a hydroquinone developer. The soft lights and shades, so dear to the heart of the photographic artist, do not in any way appeal to the spectroscopist in his scientific work. His aim is to obtain a record which approaches as nearly as possible to the resolving power of his spectrograph. The greatest test of spectrographic achievement is the resolution of the fine line structure of an absorption band group, a test far more searching than the resolution of closely situated emission lines.

Sensitisation of Plates to the Yellow, Red, and Infra-red.—We may first consider the sensitisation of plates to wave-lengths which are longer than those to which an ordinary bromide or bromide and iodide emulsion is sensitive. In 1873 H. M. Vogel found that some commercial collodion emulsion plates, to the film of which had been added a small amount of yellow dye in order to diminish halation, exhibited a different degree of sensitiveness to the solar spectrum from that of the undyed film. This observation led Vogel to the discovery that when a dye is added to a silver bromide emulsion, or when the plate is allowed to remain in a solution of the dye, the sensitivity of the emulsion is increased towards the light rays absorbed by the dye. The first dye used by Vogel was corallin, which absorbs the yellow-green rays, and it was found that its use renders the plate sensitive to these rays. Vogel tried many other dyes, including naphthalene red, fuchsine, etc., and found that in each case the plate became sensitive to the light absorbed by the dye employed. One of the dyes used by him was cyanin, a substance produced by the condensation of lepidine with quinoline, and this subsequently became of great importance.

Following on this work by Vogel, a considerable amount of further investigation was carried out with other artificial colouring matters. Thus Waterhouse showed that collodion emulsion is sensitised by eosin, and later it was found by Clayton and Tailfer that this substance also sensitises gelatine emulsions. Gelatine plates sensitised in this way were made commercially for many years under the name of isochromatic plates.

In 1884 Vogel used quinoline red for sensitising plates to the orange, yellow, and yellow-green regions, and he also prepared plates

sensitised by a mixture of quinoline red and cyanin and called them azaline plates. It is to Vogel also that we are indebted for the discovery that eosin has the strongest effect when used in the form of its silver salt dissolved in ammonia. Eder [1] carried out an extended investigation into the effects produced by various dyes, and he showed that erythrosin is better than eosin, when used in the form of its silver salt dissolved in ammonia. At the present time erythrosin is used almost exclusively in the preparation of the isochromatic and orthochromatic plates of commerce. The sensitivity curve of these plates shows a maximum at $\lambda = 5650$ and a minimum between that region and the blue.

It is useful and indeed essential to obtain a permanent and accurate record of the sensitivity curve of a photographic plate after treatment with one or other of these sensitisers, and it will be convenient here to describe a very simple instrument, which is known as the wedge spectrograph, and is in general use for this purpose. The essential construction of this instrument consists of a horizontal slit, which is illuminated by a beam of light from a continuous source concentrated by a condensing lens. The rays from the slit are rendered parallel by a collimating lens and then are diffracted by a plane transmission grating set at a small angle with the vertical and with its rulings parallel to the slit. Behind the grating is another lens which focusses the first order spectrum on to a flat photographic plate. In order to obtain a wave-length scale on the photographic negative a transparent plate with the scale photographed on it is mounted in the dark slide immediately in front of the photographic plate. When an exposure is made this scale is impressed on the spectrum photograph. In order to absorb the ultra-violet rays of the second order spectrum, the gelatine of the plate carrying the scale is dyed at the end which transmits the red of the first order. The spectrum is of course normal, and it is easy to obtain uniform intensity of the spectrum by proper adjustment of the optical system.

As described, this apparatus will not give a satisfactory record of sensitivity of the photographic plate, and to render this possible a neutral-tinted wedge is placed in front of the slit, so that a regular gradation of intensity is obtained along its length. This results in an intensity curve being recorded on the negative, which is entirely governed by the sensitivity of the plate to the different rays of the spectrum. These neutral wedges show selective absorption in the violet and ultra-violet, and consequently the intensity curve is of no value for wave-lengths smaller than about $\lambda = 4600$. This, however, is of little consequence, since we are only concerned with sensitivity measurements for wave-lengths greater than this, which is about the region of maximum sensitivity of the ordinary untreated photographic plate.

This spectrograph may also be used for obtaining a record of the

[1] *Handbuch der Photographie*, I., 226. Wilhelm Knapp, Halle, 1891.

absorption spectra of the dyes used, which is sufficiently accurate for a comparison between their absorptive power and their sensitising effect. For this purpose a wedge-shaped cell containing a solution of the dye is placed in front of the slit in place of the neutral-tinted wedge. The construction of this instrument is shown diagrammatically in Fig. 90, and the outside view is shown in Fig. 91. As an example of the sensitivity curves obtained by this wedge spectrograph, Fig. 92 shows the curve given by an orthochromatic plate which has been treated with erythrosin.

Before dealing with the next great advance in the subject, which commenced in 1904, mention may be made of the work of Higgs on the photography of the solar spectrum, which entailed the preparation of photographic plates sensitive to the yellow, orange, and red regions. The dyes used by him were alizarine blue and coerulin in the form of their bisulphite compounds, and these were found to be very successful, an experience that has been confirmed by others.

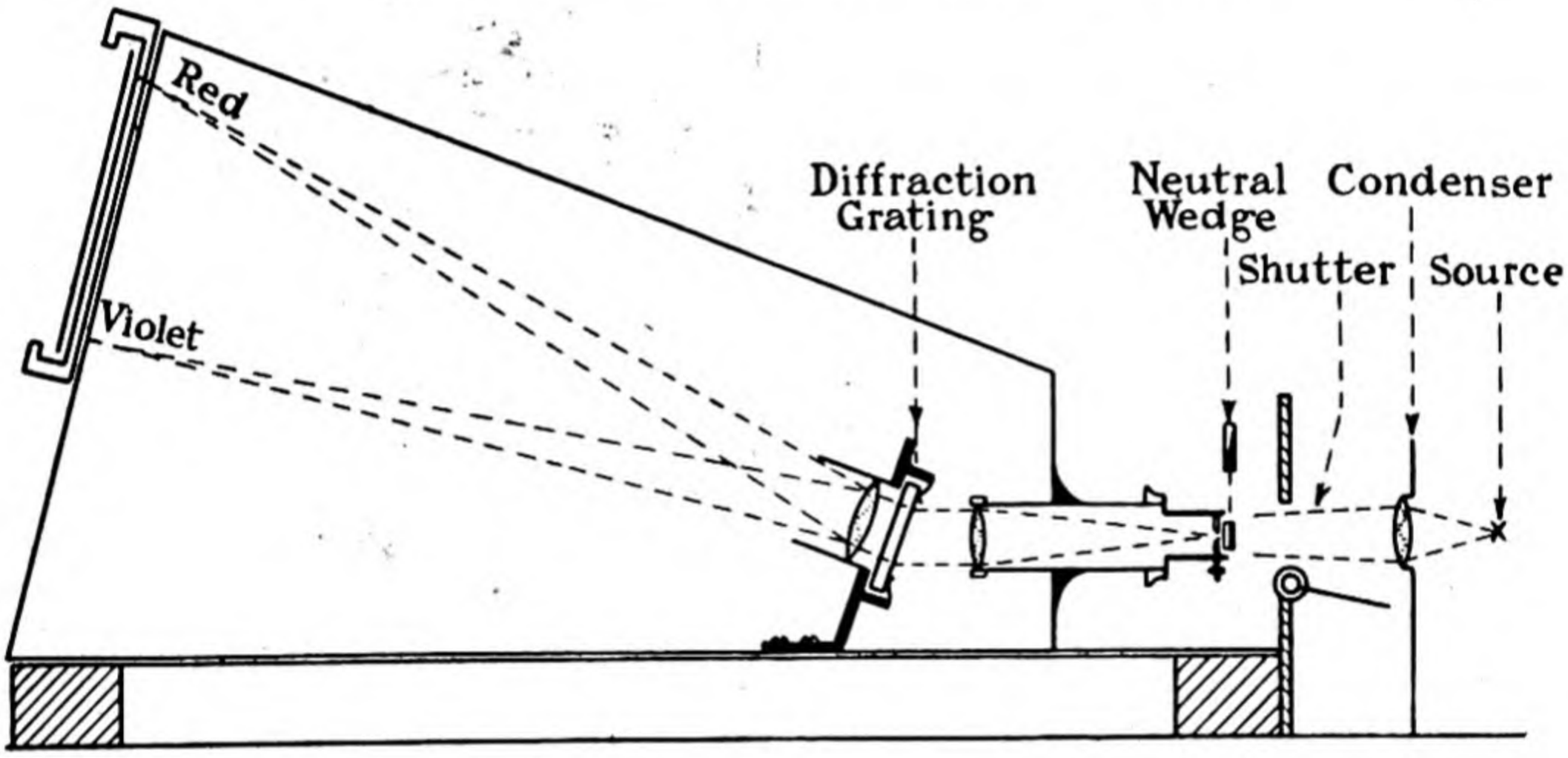


FIG. 90.

Higgs[1] gives the following rather lengthy method of preparation of the compounds, at the same time pointing out the necessity of using pure substances for the best results. He says :—

"To a saturated solution of sodium bisulphite in a mortar is added alizarin blue paste. This is disintegrated with a pestle, and poured into a glass vessel capable of holding an additional quantity of sodium bisulphite, in all 10 parts of the paste to 20 parts of the bisulphite, and another 10 parts of water. The vessel is well stoppered, set aside in a cool place for five or six weeks, and shaken daily, but left undisturbed during the last eight or ten days.

"The solution is decanted, filtered, and treated with alcohol, to precipitate the greater portion of the remaining sodium bisulphite. Fifty parts of water are now added with a sufficiency of sodium chloride to form a concentrated solution. Again set aside in an open-mounted

[1] *Proc. Roy. Soc.*, **49**, 345 (1891).

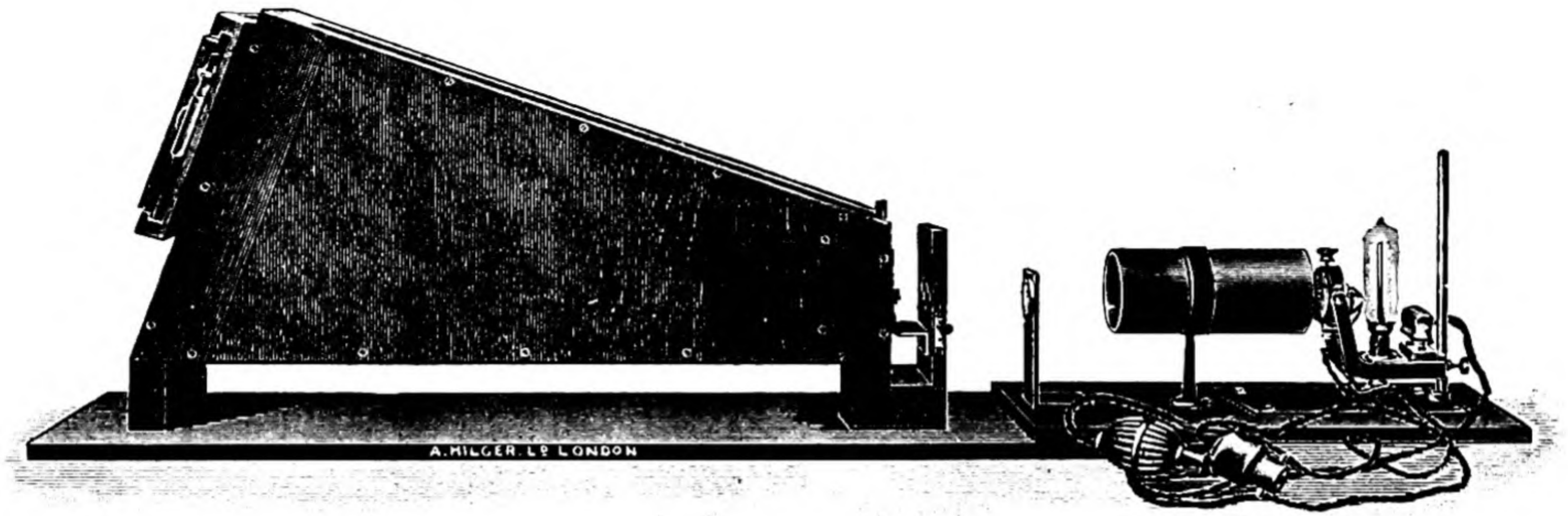


FIG. 91.

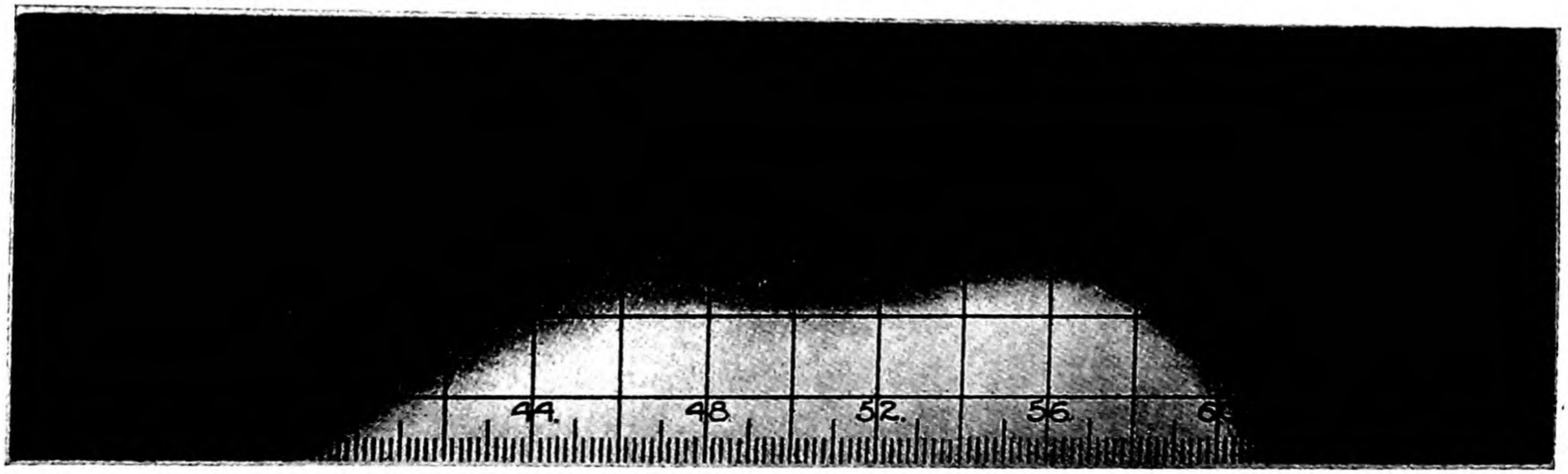


FIG. 92.

glass jar, covered with bibulous paper, for seven or eight days, a deposition of the dye in a crystalline state, together with sulphite of calcium, will take place, which latter, owing to its insolubility in water, may be removed by filtration.

"The alizarin blue S is separated from any unaltered substance left in the original stoppered vessel by solution, and added to the brine, now purified from lime salts, and once more set aside to crystallise; the final purification is effected in a beaker containing alcohol and a small percentage of water to remove the last traces of sodium chloride, collecting the crystals on a filter paper and drying at ordinary temperatures.

"The needle-shaped crystals are of a deep-red colour. Dilute solutions are of a pale sherry colour, changing with the addition of a few drops of ammonia to a green, which immediately gives way to magenta and every shade of purple till it assumes a blue colour.

"Plates immersed in a solution containing 1 : 10,000 of the dye and 1 per cent. of ammonia give the most perfect results the day after preparation, but rapidly deteriorate unless kept quite dry.

"An exposure of forty minutes with a slit width of 0·001 inch gave the region of A in the second order of a grating with perfect detail; $\lambda = 8400$ has also been reached."

The process for the preparation of pure cœrulin S is a slight modification of the preceding. The results obtained, as well as the actinic curve, are almost identical. The pure substance is almost white.

Alizarin blue bisulphite in combination with other dyes was used with considerable success by Lehmann,[1] who after making trial of several dyes, amongst which were cœrulin and cyanin, found that the following solution gave the best results :—

Alizarin blue bisulphite (1 in 500)	2 c.c.
Nigrosin (water soluble) (1 in 500)	1·5 c.c.
Ammonia (sp. g., 0·910)	1·0 c.c.
Distilled water	100 c.c.
Silver nitrate (1 in 40)	5 drops.

The solution is filtered, and the plates are soaked therein for four or five minutes, and quickly dried. As a developer, Lehmann recommended ferrous oxalate, containing 3 to 4 c.c. of potassium bromide solution to each 50 c.c. of developer. All processes should be conducted in absolute darkness, but if one prefers not to have complete darkness, light as nearly monochromatic as possible should be used of about the wave-length of Fraunhofer's E. The plates do not keep for more than four days at the longest, and are sensitive to $\lambda = 9200$, and even to $\lambda = 10{,}000$ with longer exposure. It is preferable to recrystallise the dyestuffs before using them, because the sensitiveness of the plates is materially increased thereby, especially for the longer wave-lengths.

A considerable number of other dyestuffs were employed during

[1] *Arch. f. Wissenschaftliche Photogr.*, II, 216 (1900).

this stage of the development of our knowledge, but the results are only of historical interest and need not be described. One of the compounds discovered at this time was acridine orange NO, which is still the best sensitiser for the region between $\lambda = 5000$ and $\lambda = 5400$.

A new epoch was opened in 1904 by the introduction of colouring matters which changed the whole situation. This advance commenced with the discovery by Miethe and Traube of the sensitising power of ethyl red, which is an analogue of cyanin, and is obtained by the condensation of quinaldine ethiodide with quinoline ethiodide. Miethe and Traube found that ethyl red was superior to cyanin in that the emulsions made with it were not subject to the trouble of fogging and deterioration which were characteristic of the cyanin treated plates. As the result of the researches of E. König, the Hoechst Dye Works produced in rapid succession a whole series of the isocyanin dyes, these differing from one another merely in the substituent groups. Amongst those of greatest interest may be mentioned orthochrome T, pinaverdol, and pinachrome. This series extends the sensitivity of the silver bromide emulsion to about $\lambda = 6500$, but they are essentially sensitisers for the orange and green. A true red sensitiser was not found until 1906, when Homolka of the Hoechst Dye Works discovered pinacyanol. This dye-stuff was originally prepared by the addition of formaldehyde to the alkaline condensation of quinaldine ethiodide with quinoline ethiodide, but it is now known that the quinoline does not enter into the final product and that the formaldehyde determines the reaction by supplying an extra CH group.

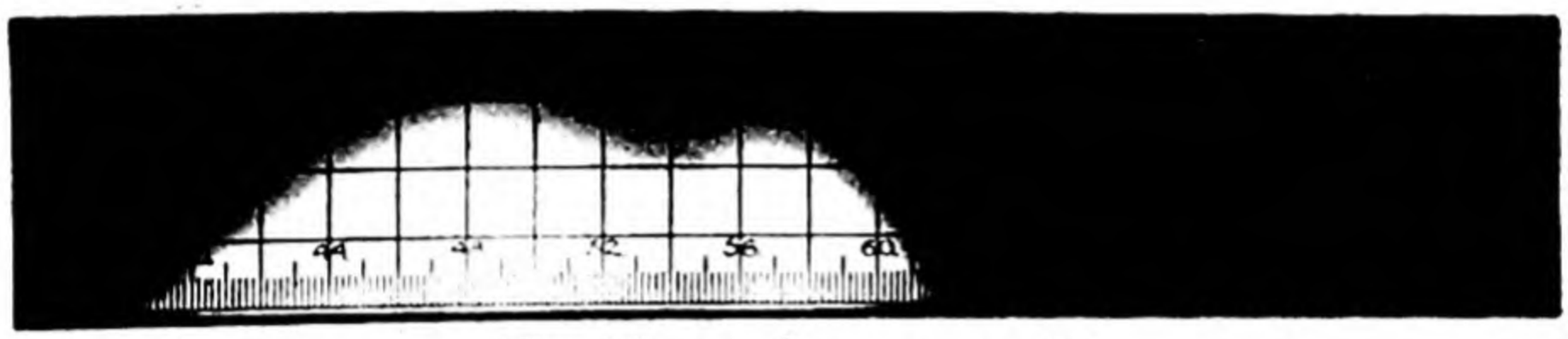
Dyes of the type of pinacyanol are known as the carbocyanins, and amongst the substituted carbocyanins may be mentioned naphthacyanol, which is prepared by the use of β-naphthaquinaldine ethiodide. This substance extends the sensitivity of the plate to about $\lambda = 7500$. Yet another dye was introduced about this time by the Hoechst Dye Works, namely, dicyanin, which is prepared by the condensation of 2·4-dimethylquinoline ethiodide with itself, with simultaneous oxidation.

The influence of this period of advance in the extension of sensitivity of the photographic plate is shown by the curves in Plates I. and II. It will be seen that with the successive use of acridine orange, erythrosin, orthochrome T, pinachrome, and pinacyanol, the sensitivity extends towards the red until with pinacyanol the whole of the visible spectrum is included within the range of the plate. By the use of pinacyanol in conjunction with a green sensitiser, such as orthochrome T, pinachrome, or pinaverdol, an emulsion can be obtained which is fully sensitive to the whole of the visible spectrum. It is in this way that the panchromatic plates and films are prepared at the present day.

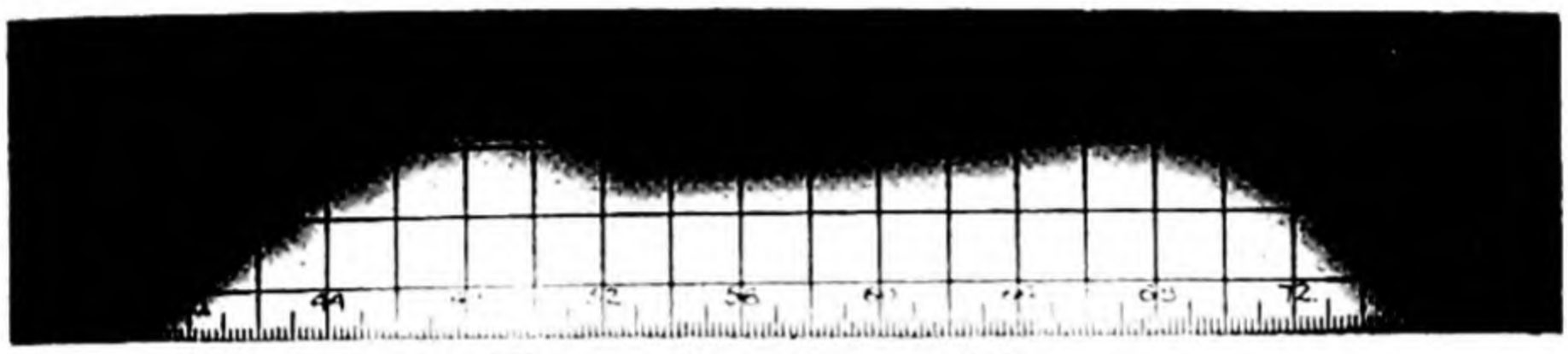
The introduction of these new dyes by the Hoechst Dye Works has proved to be of the greatest importance in practical photography, for the panchromatic emulsions prepared by their use were rapidly adopted

PLATE I.

Ordinary

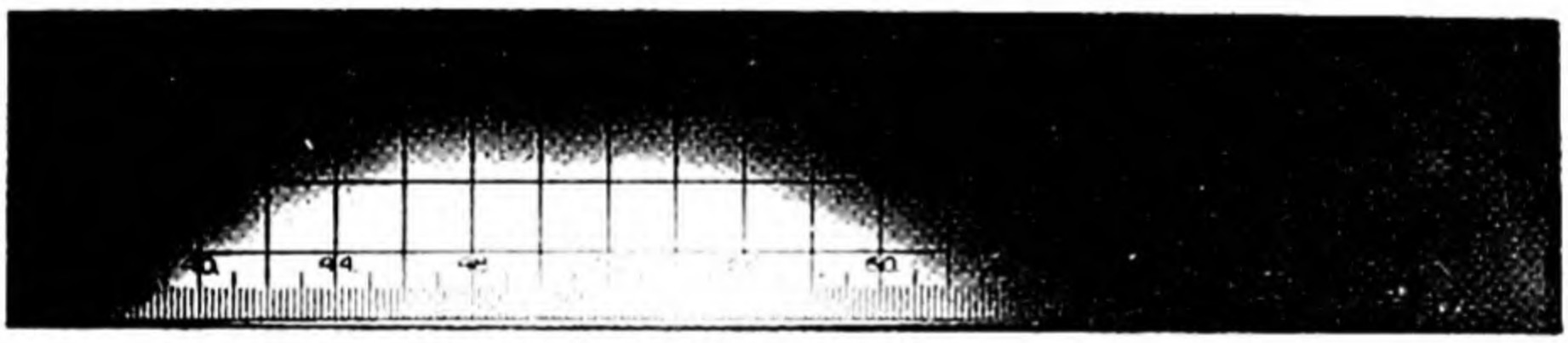


Orthochromatic

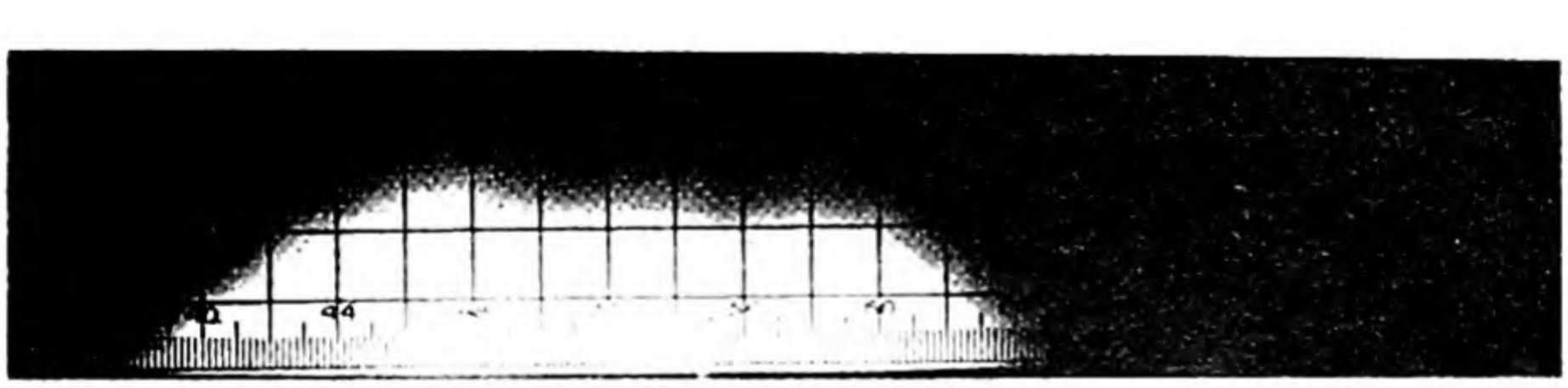


Panchromatic

Acridine Orange



Pinaflavol



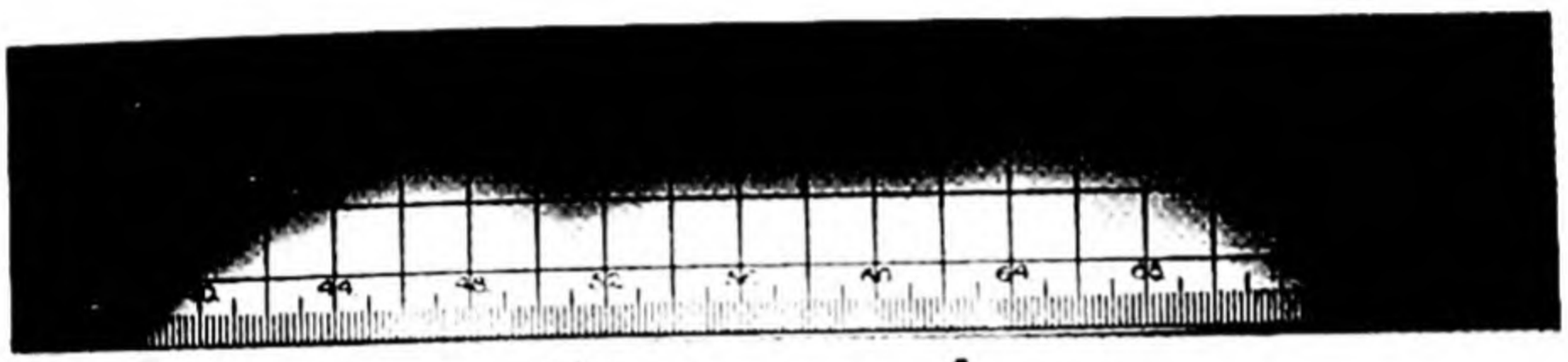
Orthochrome T

[*To face page* 362.

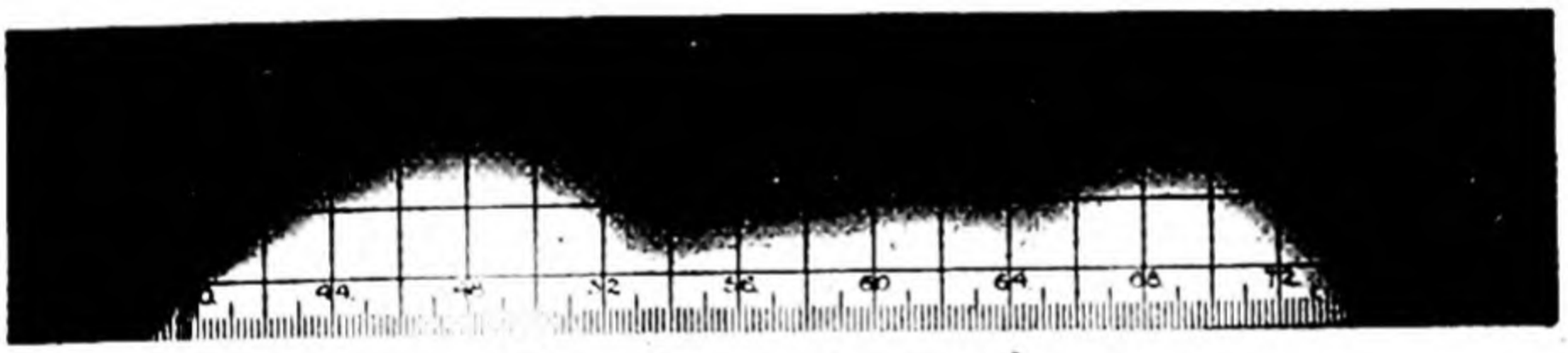
PLATE II.

Erythrosine

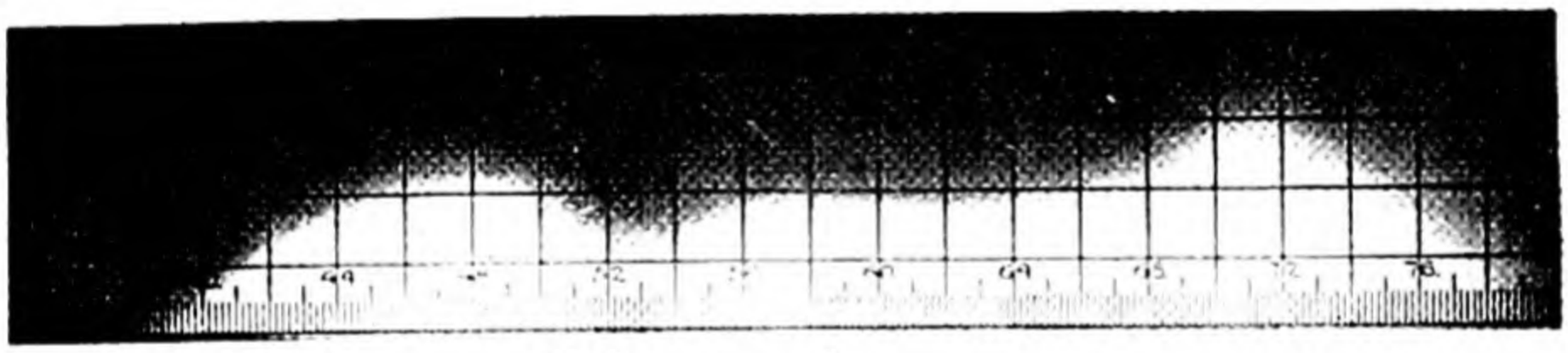
Pinachrome



Pinacyanol



Napthocyanol



Dicyanine

Kryptocyanine

[*To face page* 362.

very widely for commercial photography and also to some extent for pictorial photography. In colour photography, too, the modern methods depend essentially on the possibility of obtaining materials of a high degree of sensitivity throughout the whole visible spectrum. Modern panchromatic plates and films enable exposures of 0·2 second to be made with the proper colour filters at apertures as low as f/4·5. These short exposures are, of course, imperative in cinematography, and in aerial photography, when red filters are used to penetrate atmospheric haze. This latter work will be referred to again below.

Owing to demands caused by the great war and the special circumstances thereby created, there was great activity in England, France, and the United States, in connection with the production of colour sensitisers. In this country much work was done by Pope and his colleagues, who prepared an isocyanine dye, sensitol green, and also another, sensitol red, which was identical with pinacyanol. A third was prepared [1] by the condensation of *p*-dimethylaminobenzaldehyde with *α*-picoline methiodide. The ethiodide analogue of this was introduced under the name of pinaflavol in 1919 by the Hoechst Dye Works.

Whilst corresponding work was carried out in France,[2] the investigations in America have led to results which are of especial value in spectroscopic work. In addition to work on the isocyanins and pinacyanol,[3] important results have been obtained with two new dyes. Reference has already been made to dicyanin of the Hoechst Dye Works, and the sensitivity curve of plates treated with it was included amongst those shown in Plate II. The maximum of sensitivity is at $\lambda = 7100$, but it falls off very slowly on the long wave-length side, and both Meggers in Washington and McLennan in Toronto have succeeded in reaching $\lambda = 10{,}000$ with this material. It is, however, very unsatisfactory for two reasons. In the first place the dyed emulsion does not keep well, so that the plates must be prepared by bathing them in solutions of the dye containing alcohol and ammonia. In the second place the conditions for obtaining the best results are rather obscure, and failures often attend its use.

In 1919 Adams and Halle discovered a new dye, which they called kryptocyanin, by the condensation of lepidine in the presence of formaldehyde. This substance produces a region of strong sensitivity between $\lambda = 7000$ and $\lambda = 8000$, with maximum at $\lambda = 7700$. Its action is quite different from that of dicyanin, being quite stable, so that it can be added to the emulsion before the plates or films are coated. It is extraordinarily effective, only 1 part in 500,000 being required, which is about one-tenth of that necessary in the case of pinacyanol. Unfortunately, the sensitivity curve given by krypto-

[1] *Journ. Chem. Soc.*, **121**, 946 (1922).
[2] Lumiere and Barbier, *Bull. Soc. Chim.*, **7** (3), 182 (1920); Barbier, *Bull. Soc. Chim.*, **27**, 427 (1920).
[3] *Journ. Ind. Eng. Chem.*, **11**, 460 (1919).

cyanin falls off very rapidly on the red side of the maximum, with the result that at $\lambda = 900$ it is considerably inferior to dicyanin.

In 1925 H. T. Clarke at the Eastman Kodak laboratories noticed

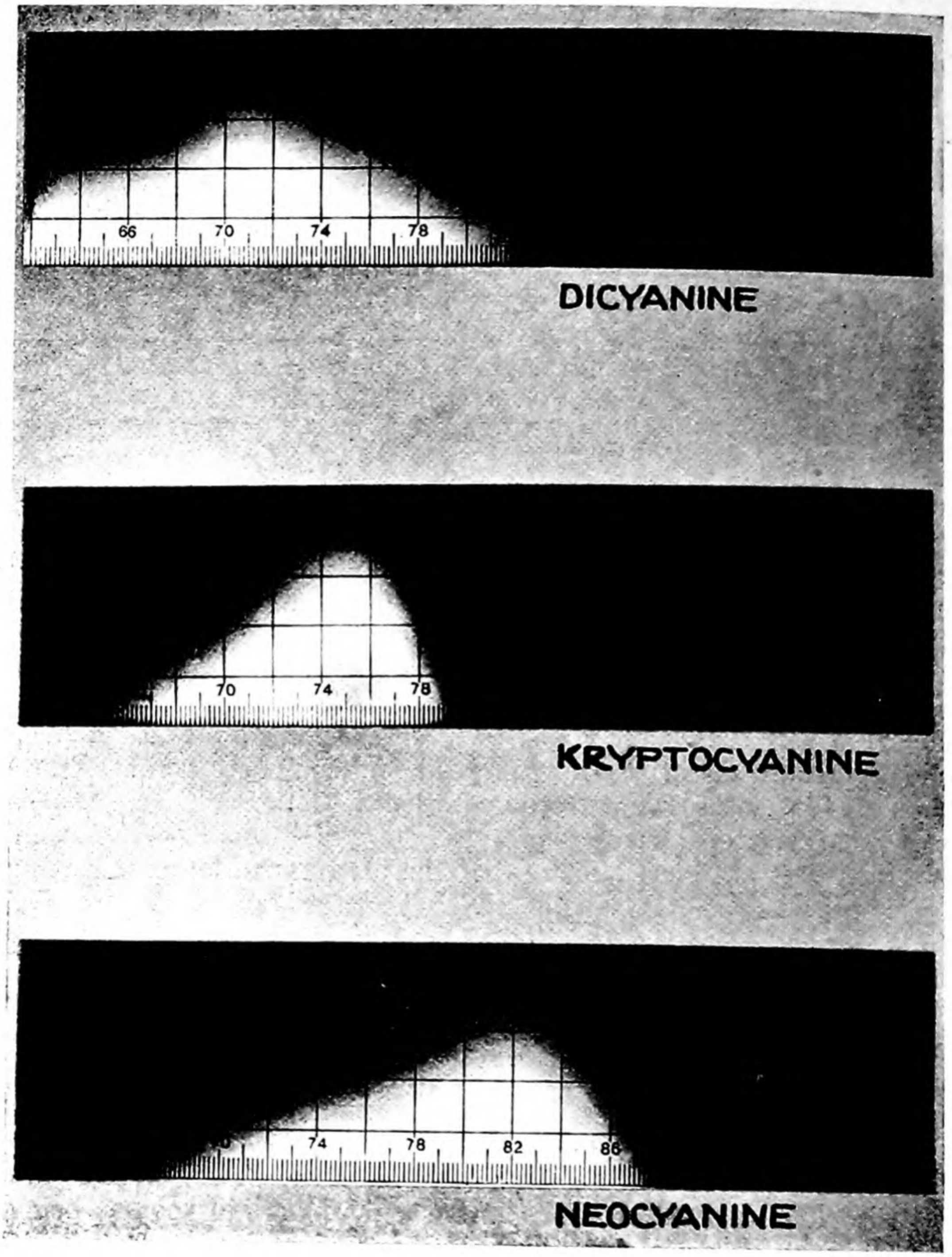
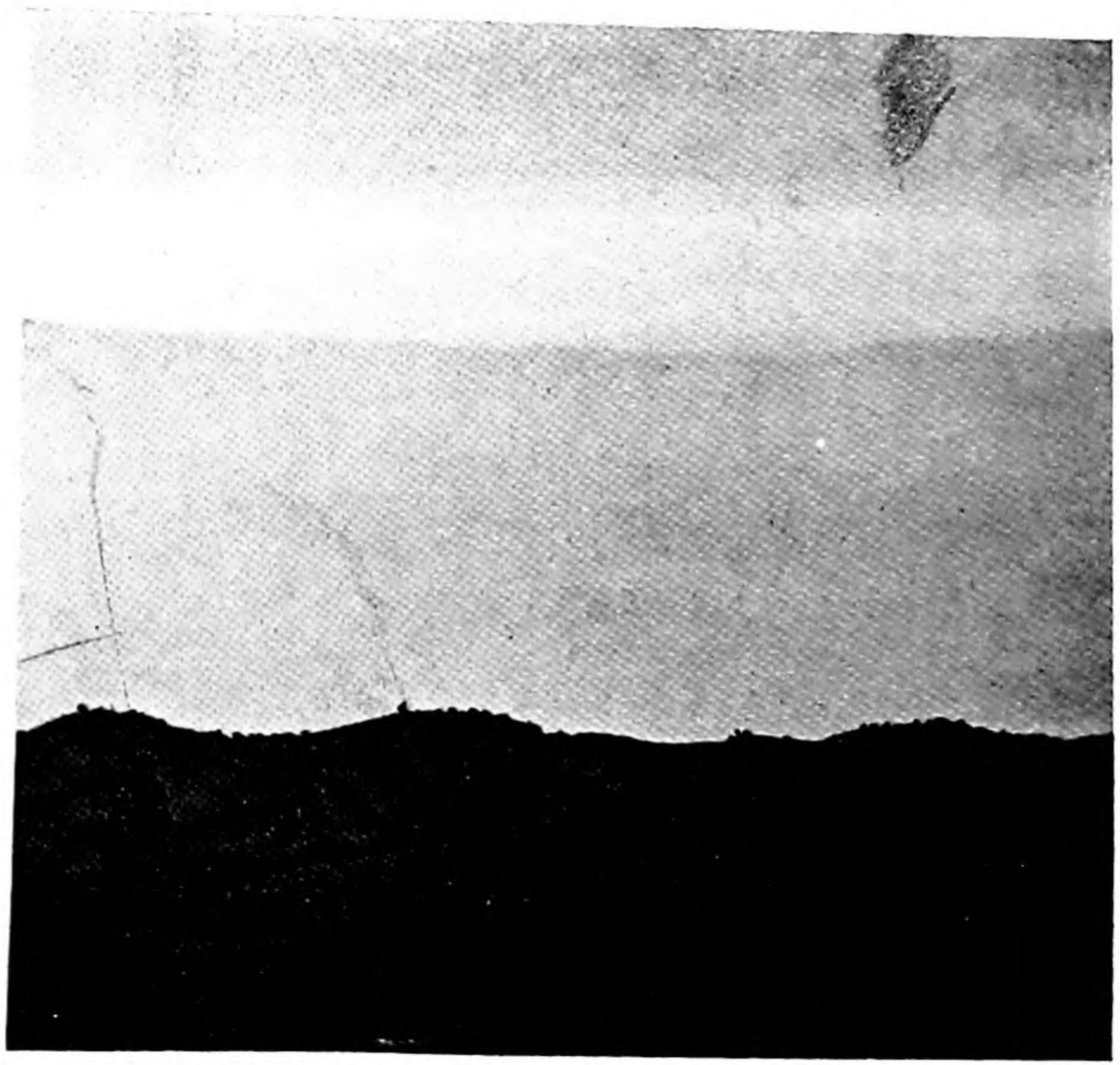


FIG. 93.

that in the preparation of kryptocyanin another dye with a smaller solubility is simultaneously formed, to which the name of neocyanin has been given. The effect of neocyanin in sensitising photographic plates has been shown by Schoen, Briggs, and Dunden to be remarkable.

PLATE III.



[*To face page* 365.

The resulting curve of sensitivity shows a maximum of about $\lambda = 8200$, and it is quite easy to reach $\lambda = 9000$ with short exposures. When its action is enhanced by ammonia, it is possible to reach $\lambda = 10{,}000$ without any difficulty.

The mercury line at $\lambda = 10{,}140$, which was first discovered by means of the thermopile, has been photographed after long exposures by McLennan and others on plates bathed with dicyanin. With neocyanin plates, hypersensitised by ammonia, this line can be photographed with exposures of less than one hour, and with exposures of about ten hours $\lambda = 11{,}290$ has been reached. The sensitivity curves of plates treated with dicyanin, kryptocyanin, and neocyanin, respectively, are shown in Fig. 93.

Reference has already been made to the high penetration through atmospheric haze obtained by the use of plates sensitive to the extreme red and a suitable colour screen. Although this is somewhat outside our present reference, yet it is not possible to pass by this modern advance in photographic technique without comment. I cannot do better than give in his own words the last part of Dr. Mees' article, for which I have already expressed my deep indebtedness.

Plate III. shows two pictures taken by Professor Wright of the Lick Observatory from the top of Mount Hamilton. The Yosemite Valley is in the extreme distance, and in the valley between, thirteen miles from Mount Hamilton, is the town of San Juan. It will be seen in the photograph taken on an ordinary plate that no trace of San Juan is visible nor can anything of course be seen of the Yosemite Valley. Only the boundary hills can be seen against the sky. In the kryptocyanin plate with a filter, the whole is perfectly clear and the Yosemite Valley, 120 miles away, can be distinguished quite clearly. Working in the less clear atmosphere of the east, we have compared neocyanin with kryptocyanin for this purpose, photographing at about twenty miles distance with a long focus lens. We took three photographs: one with an average wave-length of 6500 on a panchromatic plate with a red filter, one on kryptocyanin with a filter, and one on neocyanin with a special liquid filter giving a wave-length of 8750. The greater penetration of the kryptocyanin than the panchromatic plate is well seen, but the neocyanin plate is seen to give even greater penetration.

Dr. Wright applied this haze penetration to the photography of Mars at the last opposition, photographing the planet on an ordinary plate and also upon a kryptocyanin plate with a filter, and he obtained the very remarkable result shown in Fig. 94. It is seen that the image of the planet by violet light is actually considerably larger than in the photograph taken by infra-red light. All corrections were made for other optical effects, and it was concluded that this enlargement was due to the scattering of the shorter waves by the atmosphere of Mars, a photograph taken by violet light representing the outside of the atmosphere of Mars, whilst a photograph taken on the kryptocyanin plate represents the surface of the planet. This is borne out of course

by the markings of the surface, which are well shown in the kryptocyanin plate, whilst they are practically invisible in the violet photograph. The result of this work has been to change the view-point of astronomers with regard to the atmosphere of Mars. It had always been thought that Mars either had no atmosphere at all or a very shallow one. It appears now that the atmosphere of Mars is about 120 miles deep, which is just about what that of the earth would be owing to the lower gravitational properties of that planet. It has probably not a dense atmosphere though it is largely devoid of water vapour. The characteristic difference between Mars and the earth is not the absence of air from Mars, but the much smaller amount of water found on Mars, which leads to an absence of liquid seas and to a smaller degree of cloudiness. It is possible that the scattering power of Mars is not due to water vapour or even to the molecules of gas, but to dust. A nearly waterless planet whose components are represented by large, high, plateau-like deserts would probably throw into the air vast quantities of yellowish dust, and it is not improbable that it is this which gives the characteristic colour to the planet.

FIG. 94.

Partly as a consequence of the great extension of the spectrum which is possible with photographic as compared with visual observation photography is tending more and more to supplant the eye as an observing instrument for scientific work. Owing to the fact that refracting telescopes are corrected for visual use, the plates used are generally those sensitised with erythrosin, and a yellow filter is used to remove the blue, so that the photograph is made in the photo-visual maximum. Comparisons are made upon the magnitude of stars as recorded by violet light and by this photo-visual light with an average wave-length of $\lambda = 5600$. The ratio of the magnitudes is termed the colour index, and this has been used very largely as the means of classifying stars, the stellar classes which depend primarily upon the spectrum, being indicated by the magnitude of the colour index. In view of the availability of kryptocyanin, it seems not unlikely that in the future another measurement will be made with an average wave-length of $\lambda = 7500$, thus enabling better classification to be obtained without actual measurements of the spectrum.

The spectroscope has, of course, been a photographic instrument almost from the beginning, the visual spectroscopes being little more than toys. Until quite recently, however, the microscope has remained

a visual instrument, the photomicrographic methods being employed only to depict what had already been seen. It seems likely that before long the microscope in its turn will become a photographic instrument, the visual observation being used only as a guide to the photography of the unseen. The reason for this is the necessity for greater resolving power, especially in connection with the photography of the smaller organisms which are classed as filter-passing bacteria and bacteriophages. The distance between two lines which can just be seen separated is given by the equation,

$$d = \lambda/2\mathrm{NA},$$

that is to say, the distance is equal to the wave-length divided by twice the numerical aperture. Now we have probably reached the limits of numerical aperture when we use oil immersion objectives with a numerical aperture of 1·4. It is only by the use of special mounts that we can employ monobromonaphthalene immersion at an aperture of 1·6, and this is very limited in its application. In order to get increased resolving power, therefore, the only path that lies open before us is to diminish the wave-length.

In the interesting work of Barnard and Gye on the cancer virus, Barnard made use of the ultra-violet microscope developed by Kohler of Zeiss, using a wave-length of 2570 and a numerical aperture of 1·25, and obtained a resolving power of 0·11 as compared with 0·2 available to the eye working with a wave-length of 5600 and a numerical aperture of 1·4, or 0·16 available photographically by the use of $\lambda = 4500$ with the same objective.

It is perhaps questionable whether the use of the quartz instrument is worth while for the gain it gives. If photographs are taken with wave-length $\lambda = 3560$ (mercury line) and a numerical aperture of 1·4, a resolving power of 0·129 is available and the difference between 0·13 and 0·11 scarcely seems to justify the great difficulty involved in making the whole system of quartz. Barnard, however, is undoubtedly trying to get shorter wave-lengths, and if he could use a wave-length of 1850 with a numerical aperture of 1·25 he would get 0·075 resolving power, and that might be an advance of the utmost importance for bacteriology. Of course this involves a great deal of difficulty. The line at $\lambda = 1850$ given by the aluminium spark or the mercury arc is readily absorbed by air, and consequently the whole instrument from the source to the photographic plate might have to be worked in vacuum. Quartz has a considerable absorptive power and it may be necessary to construct some parts of the instrument of fluorite. The difficulties are many but the end is worth while.

Sensitising Plates by Bathing.—In addition to the foregoing, Dr. Mees has also had the great kindness to give me a report on the use of the various dyes for the sensitising of plates. This is included here for the benefit of those who wish to sensitise their own plates, it being remembered that the orthochromatic and panchromatic plates now on the market are obtained by introducing pinacyanol, together

with some yellow-green sensitising dye such as pinachrome or orthochrome T, into the emulsion before the plates or films are coated.

I. Hints on Plate Bathing.

A. General Considerations.

The aim in bathing a plate is to get a certain required amount of sensitising dye into intimate contact with the silver bromide grains of an emulsion without leaving an excess in the gelatine and especially without leaving any precipitated dye or scum on the surface. Each dye behaves differently and the optimum conditions for sensitising are determined by at least four interdependent factors: (*a*) concentration of the dye, (*b*) nature of the solvent, (*c*) temperature of the solution, and (*d*) time of bathing.

The concentration varies from 1 in 10,000 to 1 in 1,000,000, according to the dye used. Also some dyes require the use of alcohol in the dye bath, whilst others work best in a pure water solution. Temperatures from 15° to 20° have been recommended, but there is less trouble from fog and just as good sensitising in the colder solutions. Although the diffusion of the dye into the gelatine takes place more slowly in the cold, this seems to be compensated by the decreased swelling and the more rapid drying which results. The time of bathing depends both on the particular dye and the type of solution in which it is used. In many solutions the dye becomes concentrated at the surface, forming a visible scum, and if this comes into contact with a plate as it is being wetted it adheres tenaciously and is difficult to remove. Wetting the plate in water before putting it into the sensitising solution is advantageous when this occurs. A smeary fog is produced if a plate is dried with a scum of dye on the surface. In some cases it is very desirable to rinse the plate in alcohol before drying in order to remove the excess dye which may be precipitated on the surface. The use of an alcohol rinse also removes the excess of water and shortens the time required for drying.

The sensitivity conferred by certain dyes is increased by the use of ammonia or other alkali, either in the sensitising solution or as a subsequent bath. When added to the sensitising solution it causes flocculation of the dye, and more alcohol must be added to prevent the precipitation. In most cases it is more satisfactory to use the ammonia (4 per cent. by volume of 28 per cent. ammonia) or borax (2 per cent.) as a subsequent hypersensitising bath. Dicyanin A is an exception, as the ammonia in the bath seems to be more effective.

Different brands of plates may require slightly different treatment for the best results. It is advisable to use a plate of medium speed and low fog such as Eastman 40. Eastman 33 plates have more contrast and less fog and for some purposes may be preferable.

B. Method of Manipulation.

(i) *Apparatus.*—

Absolute cleanliness is the first essential in sensitising photographic emulsions. Traces of old dye solutions are certain to cause either fog or de-sensitised spots. Washing with water is not sufficient to remove the dyes absorbed on the walls of the vessels, and the use of alcohol or an acid cleaning solution is essential. Glass trays are most desirable because of the ease with which they can be kept clean. Glass baking dishes are very convenient for this purpose, since the higher walls diminish the tendency to spill the solutions when working in the dark.

(ii) *Bathing Technique.*—

A plate should be put in the dye solution in such a way as to cover the entire surface in one sweep, and the plate should be agitated during the bathing process. This can be done by rocking the tray, or better still by frequently lifting one corner of the plate with the finger nail so as to cause a violent rush of solution over the surface. Such agitation tends to prevent the precipitation of the dye on the surface and promotes more rapid sensitisation. Agitation of course in the rinse bath is essential.

After bathing the plate may be held up to drain for ten or fifteen seconds, and with small plates a violent shake before putting them in the drying rack may help to remove the drops of liquid hanging on the edge. After the plate has drained to one edge, the same edge must be kept down in the drying rack as otherwise the excess of liquid will run back causing a bad streak from one-quarter to one-half inch wide.

(iii) *Drying.*—

In general, rapid drying is conducive to high sensitivity and low fog, and with some dyes is absolutely essential. A drying cabinet with control temperature and humidity is desirable but not necessary. An ordinary electric fan in a dark room placed three or four feet from the drying rack with the blast of air directed parallel or at a slight angle to the face of the plate, gives excellent results. In this way after an alcohol rinse, plates can often be dried in from two to five minutes. When quick drying is essential the best results are obtained on a day when the relative humidity is low.

C. Preparation of Dye Solutions.

Most sensitising dyes are dissolved for use by making a stock solution, and generally speaking pure methyl alcohol is the best solvent. Erythrosin and acridin orange are more soluble in water. The stock solution is usually made to a concentration of one part of dye in 1000 parts of solution. Dicyanin A however is easily soluble only to the extent of one part in 5000 parts of methyl alcohol. It may be necessary to warm the alcohol to get the dye to dissolve in a reasonable length of time. The stock solution should be filtered in order to

remove small undissolved particles which might cause specks on the plate.

When plates are sensitised only occasionally it is advisable to make up the stock solution in very small quantities as needed rather than keep it for a very long time. Solutions of sensitising dyes are all light sensitive and must be kept in the dark. Clear glass bottles which can easily be inspected for cleanliness and then covered with black paper are satisfactory. The required amount of stock solution should be added to the cooled water or alcohol-water mixture immediately before use.

II. Instructions for Using Various Dyes.

The following processes for the various dyes have been found to give satisfactory results, although equally good results might have been obtained in a different way. In the experiments leading to these instructions the sensitising and rinse baths were used at 15° to 17°.

Acridin Orange.

Stock solution	. . .	1 : 1000 in water.
Sensitising bath	. . .	100 c.c. water.
		4 ,, stock solution

Bathe 4 minutes and dry.

Pinaflavol.

Stock solution	. . .	1 : 1000 in methyl alcohol.
Sensitising bath	. . .	100 c.c. water.
		3 ,, stock solution.

Bathe 2 minutes and dry.

Pinachrome, Pinaverdol, Orthochrome T, and Pinacyanol.

Stock solution	. . .	1 : 1000 in methyl alcohol.
Sensitising bath	. . .	100 c.c. water.
		2 ,, stock solution.

Bathe 3 to 4 minutes, rinse 1 minute in methyl alcohol and dry. An alternative method is to use 25 per cent. methyl alcohol in the dye bath, bathe 3 to 4 minutes, rinse 15 to 30 seconds or not at all, and dry.

Naphthacyanol.

Naphthacyanol is difficultly soluble and will not sensitise without a large percentage of alcohol in the bath. It is less soluble in ethyl than in methyl alcohol.

Stock solution 1 : 5000 in methyl alcohol. A more concentrated solution can be made, but the dye dissolves very slowly even in warm alcohol.

Sensitising bath	50 c.c. water.
	40 ,, methyl alcohol.
	10 ,, stock solution.

Bathe 5 minutes, rinse 1 minute in methyl alcohol and dry.

Kryptocyanin.

Kryptocyanin must be used in much lower concentration than most dyes or decreased sensitivity and fog will result. Satisfactory results can be obtained by bathing for 45 seconds in a water solution of a concentration 1 : 500,000, followed by a 30 seconds rinse in alcohol. However, the following method is better.

Stock solution . .	1 : 2000 in methyl alcohol.
Sensitising bath . .	500 c.c. water.
	1 ,, stock solution.
	2 ,, of a 1 per cent. solution of acetic acid.

Just sufficient acetic acid should be stirred into the dye solution to decolorise it within 2 or 3 minutes. Bathe for 1 minute in the sensitising bath, rinse for 1 minute in a 2 per cent. borax solution and dry. A solution of ammonia (4 c.c. of 28 per cent. ammonia in 100 c.c. of water) may be used in place of the borax, but the film does not keep nearly so well and the sensitivity is not appreciably greater. If desired the plates may be dried after bathing for 1 minute in the sensitising bath, and then hypersensitised in alkali at some later time.

Dicyanin A.

Dicyanin is very erratic in its behaviour and the directions should be followed closely in order to get good results. Even the solid dye should be kept in a cold dark place. In order to get good sensitising, ammonia must be added to the dye bath and this tends to produce heavy fog. If sensitivity must be sacrificed for the sake of getting cleaner plates, less ammonia than that recommended may be used.

The sensitising bath can only be used for a few plates as the dye soon precipitates from the solution.

Stock solution . . .	1 : 5000 in methyl alcohol (filtered).
Sensitising bath . . .	60 c.c. water.
	20 ,, methyl alcohol.
	20 ,, stock solution.
	4 ,, ammonia (28 per cent.).

Mix the water and alcohol and cool to 10°. Add the stock solution and cool the whole solution to 10°. Wait about 5 minutes for the dye to get thoroughly mixed and then stir in the ammonia. Again wait 3 or 4 minutes before using.

Bathe 4 minutes with constant agitation, drain 10 to 15 seconds, rinse 45 seconds in methyl alcohol and dry rapidly. The plates should be dried within 5 minutes.

This procedure is very similar to that used by Merrill[1] and recommended by Walters and Davies,[2] except that they use pure ethyl alcohol both for making the stock solution and in the sensitising bath.

Neocyanin.

Stock solution	. . .	1 : 2000 in methyl alcohol.
Sensitising bath	. . .	75 c.c. water.
		25 ,, methyl alcohol.
		1 ,, stock solution.

Bathe for 1 minute, rinse 30 seconds in methyl alcohol, and dry as rapidly as possible. The best results are obtained if the plates dry in about 1 minute.

Although no advantage was found in the use of ammonia in the sensitising bath, the infra-red sensitivity of the neocyanin plate can be very greatly increased by subsequent hypersensitising.

Hypersensitising solution	.	100 c.c. water.
		4 ,, ammonia (28 per cent.).

Bathe for 45 seconds and dry rapidly. Plates hypersensitised with ammonia do not keep for more than a few days.

Rhodamine B Iodide.

Stock solution	. . .	1 : 1000 in methyl alcohol.
Sensitising bath	. . .	100 c.c. water.
		10 ,, stock solution.

Wash with water 1 minute, bathe 3 or 4 minutes and dry. Rhodamine B gives very clean plates and has no apparent tendency to fog.

Pinachrome Violet.

Stock solution	. . .	1 : 1000 in methyl alcohol.
Sensitising bath	. . .	100 c.c. water
		2 ,, stock solution.

Bathe 3 or 4 minutes, rinse 30 seconds in methyl alcohol and dry. A bath containing alcohol may be used without a subsequent rinse. Pinachrome violet has a great tendency to fog.

Quinaldine Red.

Stock solution	. . .	1 : 1000 in methyl alcohol.
Sensitising bath	. . .	75 c.c. water.
		25 ,, methyl alcohol.
		4 ,, stock solution.

Bathe 5 minutes, rinse 30 seconds in methyl alcohol and dry. Quinaldine red has some tendency to fog if not used carefully.

[1] *Bull. Bureau of Standards*, No. 318, p. 487 (1918).
[2] *Bureau of Standards, Scientific Papers*, No. 422, p. 366 (1921).

Erythrosin Silver.

Sensitising bath	. . .	**100 c.c. water.**
		10 ,, stock solution.

Dissolve 0·1 gram of erythrosin in 100 c.c. of hot distilled water, add dilute silver nitrate solution as long as a precipitate continues to form, filter and wash the precipitate with water on the filter until the wash water is free from silver, *i.e.* until it gives no turbidity with hydrochloric acid. Dissolve the precipitate on the filter by pouring over it the solution of 5 or 6 c.c. of ammonia (28 per cent.) in 50 c.c. of water, and if necessary passing the filtrate again through the filter. This makes a stock solution containing about 1 : 500 of erythrosin. It should be prepared in subdued artificial light and kept in the dark. Soak plates 2 minutes in water, bathe 3 to 4 minutes, rinse in water 3 to 4 minutes and dry. Slightly more sensitising with a slight fog can be obtained by adding about 2 per cent. ammonia to the preliminary wash water and to the sensitising bath. Results obtained by this method are only very slightly better than can be obtained by the simple ammonia erythrosin bath.

Erythrosin.

Stock solution	. . .	1 : 100 in water.
Sensitising bath	. . .	100 c.c. water.
		20 ,, stock solution.
		2 ,, ammonia (28 per cent.).

Give the plates a pre-bath for 2 minutes in a solution of 2 c.c. of ammonia in 100 c.c. of water, then bathe for 2 or 3 minutes, wash in water for about 3 minutes and dry.

Borax cannot be used in place of ammonia for increasing the sensitising action of erythrosin.

Special Methods of Photography in the Red and Infra-red.—A remarkable contribution to our knowledge of the photochemistry of silver bromide emulsions was made by Abney, who succeeded in preparing a special photographic emulsion which was sensitive to rays with a wave-length of $\lambda = 20{,}000$, and by means of this has photographed the solar spectrum to $\lambda = 10{,}000$ A.U. Abney commenced his work upon the dyeing of plates, and found that the maximum of sensibility always lay in the same spectral region as the absorption maximum of the dyed emulsion. Arguing from these results, Abney [1] conceived the idea of making a silver emulsion, which of itself should absorb red light, in distinction from the ordinary emulsions which absorb blue light, and hence appear red by transmitted light. This he succeeded in doing, and obtained an emulsion essentially blue by transmitted light, which was extremely sensitive to red rays, even in some cases to the rays from boiling water. Before describing the methods employed, it may be pointed out that Abney found that

[1] *Phil. Trans.*, **171**, II., 653 (1880).

his emulsion had two maxima of sensitiveness, one at $\lambda = 7600$, and the other at $\lambda = 3800$; and he therefore suggested, as one maximum was the octave of the other, that the silver bromide which is blue by transmitted light is more associated than the bromide which is red. He also found that the new emulsion when rubbed became converted into the ordinary variety, red by transmitted light, and lost its power of responding to the longer wave-lengths.[1] The following method was given by Abney :—

A normal collodion is first made according to the formula—

Pyroxylin (any ordinary kind)	16 grains.
Ether (sp. gr., 0·725)	4 ozs.
Alcohol (sp. gr., 0·820)	2 ,,

This is mixed some days before it is required for use, and any undissolved particles allowed to settle, and the top portion is decanted off. Three hundred and twenty grains of pure zinc bromide are dissolved in ½ to 1 oz. of alcohol (0·820), together with 1 drachm of nitric acid. This is added to 3 ozs. of the above normal collodion, which is subsequently filtered. Five hundred grains of silver nitrate are next dissolved in the smallest quantity of hot distilled water, and 1 oz. of boiling alcohol added. This solution is gradually poured into the bromised collodion, stirring briskly while the addition is being made. Silver bromide is now suspended in a fine state of division in the collodion, and if a drop of the fluid be examined by transmitted light it will be found to be of an orange colour.

Besides the suspended silver bromide, the collodion contains zinc nitrate, a little silver nitrate, and nitric acid, and these have to be eliminated. The collodion emulsion is turned out into a glass flask, and the solvents carefully distilled over with the aid of a water bath, stopping the operation when the whole solids deposit at the bottom of the flask. Any liquid remaining is carefully drained off, and the flask filled with distilled water. After remaining a quarter of an hour the contents of the flask are poured into a well-washed linen bag, and the solids squeezed as dry as possible. The bag with the solids is again immersed in water, all lumps being previously crushed, and after half an hour the squeezing is repeated. This operation is continued until the wash water contains no trace of acid when tested by litmus paper. The squeezed solids are then immersed in alcohol (0·820) for half an hour to eliminate almost every trace of water, when, after wringing out as much as possible of the alcohol, the contents of the bag are transferred to a bottle, and 2 ozs. of ether (0·720) and 2 ozs. of alcohol (0·805) are added. This dissolves the pyroxylin, and leaves an emulsion of silver bromide, which when viewed in a film is essentially blue by transmitted light.

All these operations must be conducted in very weak red light,

[1] This observation is not without interest in connection with the existence of an activated state and its destruction by rubbing discussed in the previous chapter under the name of triboluminescence.

such a light, for instance, as is thrown by a candle shaded by ruby glass, at a distance of 20 feet. It is pointed out in a footnote that a faint green light of a wave-length midway between E and D would be best.

It is most important that the final washing should be conducted almost in darkness. It is essential to eliminate all traces of nitric acid, as it retards the action of light on the bromide, and may destroy it if present in appreciable quantities. To prepare the plate with this silver bromide emulsion, all that is necessary is to pour it over a clean glass plate, as in ordinary photographic processes, and to allow it to dry in a dark cupboard. (It has been found advantageous to coat the plate in red light, and then to wash the plate and immerse it in a dilute solution of hydrochloric acid, and again wash, and finally dry. These last operations can be done in dishes in absolute darkness; the hydrochloric acid gets rid of any silver sub-bromide which may have been formed by the action of the red light.)

Abney recommends the ferrous oxalate developer mixed with an equal volume of potassium bromide solution containing 20 grains to the ounce. The film is first softened by flowing over it a mixture of equal parts of alcohol and water, and is then well washed. The developer is now poured over the plate, taking care not to touch the film with the fingers.

By diminishing the amount of nitric acid to one-fourth the amount given above, it is possible in very cold weather to obtain plates which are sensitive to the radiations from boiling mercury or even boiling water. In summer-time this emulsion produces what is known as foggy pictures; but it can be rendered of use by flooding with hydrochloric acid. In the preparation of such an emulsion the water bath must be kept at a temperature but little above that of the boiling-point of ether.

Ritz [1] varied the proportions of Abney's mixture, and in all cases found that the sensibility is much increased when the silver nitrate or bromide is in excess. It is preferable to use the latter. An emulsion obtained by means of concentrated solutions of silver nitrate and zinc or ammonium bromide, reducing the quantity of pyroxyline almost to vanishing point, is more sensitive than emulsions prepared in the usual way. The characteristics of such an emulsion are: (1) the greatest concentration possible of the reacting solutions; (2) the minimum possible of the pyroxyline, with reasonable precautions; (3) the formation of a homogeneous emulsion.

The bromides of zinc and ammonium act in an almost similar way, and we can also replace the mixture of alcohol and ether by methyl alcohol or acetone. The transformation of the silver bromide is then of a purely physical order, and is always accompanied by an increase in the diameter of the grains. Finally, the emulsion is submitted to pressure at about 100° C. for one hour, and at 40° C. for

[1] *Comptes Rendus*, **143**, 167 (1906).

twenty-four hours. Still, however, Ritz found that Abney's limit was not passed, the bromide becoming granular and decomposing under the influence of longer wave-length radiation.

He therefore found it better, after having distilled the ether, to allow it to cool; then return it to the mixture and once more distil. He could then use solutions two or three times weaker than those employed by Abney, and so obtain much more homogeneous emulsions. It was also found that the sensitiveness to white light is increased to a slight degree.

It is known that under the action of heat an emulsion of gelatine bromide becomes much more sensitive to the very refrangible rays, but less so to the yellow and red. Ritz also found that the variations in the concentrations of the salts and of the gelatine have the same influence as in Abney's emulsion. This leads to the conclusion that this characteristic is a quantitative difference only of the same property of silver bromide. He performed the following experiment to confirm this theory. A precipitate of silver bromide, obtained either in water or in alcohol, was washed and heated for some minutes under pure water, or, if found to be more advantageous, water with a few drops of silver nitrate added. After emulsification in gelatine and a further action of heat, plates more sensitive to infra-red radiations than those of Abney were given. After 5 minutes' exposure to the spectrum of a Nernst lamp much less rich in heat-rays than the sunlight used by Abney, a spectrum was shown which decreased regularly from the blue end to $1{\cdot}4\mu$ without showing any of the rough variations of plates treated with dyes. The characteristic blue colour of Abney's emulsion appeared in this case immediately, and in the cold.

In 1840 Herschel found that if photographic materials which had been exposed to blue light were subsequently exposed to red light, a positive was obtained by reversal of the first exposure. Draper also found that if a Daguerreotype plate during exposure to the spectrum were also exposed to faint white light, the extreme red portion was recorded as reversed. Waterhouse showed that this reversing effect of red light was also obtained with collodion plates and, further, that the action was greatly increased by staining the plates with certain dyes. Millochau [1] applied this method with some success in the following way. Very rapid silver bromide gelatine plates are immersed for 10 minutes in distilled water which contains a few drops of acetic acid, and then are placed for the same time in a saturated alcoholic solution of malachite green. The plates are then rinsed rapidly and dried, the whole process being carried out in the dark. When required for use, the plates are first exposed for thirty seconds to a four candle-power electric lamp at 75 cm. distance, and are then exposed in the spectrograph. With these plates Millochau succeeded in photographing the solar spectrum from $\lambda = 7500$ to $\lambda = 9500$. Trials were also made with these plates in a spectrograph of low dispersion, and

[1] *Comptes Rendus*, **144**, 725 (1907).

it was found that the inverse action extends from $\lambda = 6000$ to as far in the infra-red as the optical parts of the instrument allowed.

When Luppo-Cramer [1] discovered the de-sensitising action of the azine dyes, he found that with plates, which had been treated with one of these, a latent image was destroyed by exposure to the red light of a dark-room lamp. The practical use of these azine dyes and also those of the phenyl methane group was extended by Terenin,[2] who succeeded in photographing the mercury line at $\lambda = 11{,}280$.

A full discussion of the whole subject is given by Carroll,[3] who studied in this connection the action of a number of dyes and inorganic materials. He found that the practical limit of work with this process is about the same as that given by plates sensitised by means of dicyanin. Carroll confirmed the observations of previous observers as to the great efficacy of the azine and phenyl methane dyes, and obtained the best results with malachite green. The wave-length of the light in the preliminary exposure is unimportant, but the length of exposure should be chosen with care, the best results being gained by an exposure which would give a density of unity on development. The plate is bathed in a 0·1 per cent. solution of malachite green made acid by the addition of 2 per cent. hydrochloric, nitric, or sulphuric acid.

Carroll suggests that the results are to be explained by an oxidation theory of de-sensitisation. He states that "the dyes in the dark or in visible illumination have an oxidation potential sufficient to prevent formation of new latent images. On activation by light of their characteristic frequency, their potential is raised sufficiently to cause destruction of the latent image already existing."

On the other hand, there would seem to be a marked analogy between these results and those of phosphorescence recorded in the preceding chapter. In each case a new condition is established by exposure to light and in each this new condition is discharged by red and infra-red light. It may therefore be suggested that the latent image produced on a photographic plate by exposure to light is an activated state which is similar to that established in a phosphore by light. The energy increment in each case is discharged by the red and infra-red light, the effect being to bring the activated state into a condition of instability similar to that produced by an increase in temperature.

Lehmann [4] succeeded in photographing the spectrum as far as 20,000 Ångström units by means of the phosphoro-photographic process. This process depends upon the property possessed by infra-red rays of extinguishing the phosphorescence of certain substances. Very finely powdered zinc sulphide (which possesses a green phosphorescence) is pressed by means of a glass plate into a film of

[1] *Der Photographie*, p. 368, 1920; *Negativ-Entwicklung bei hellem Lichte*, p. 182, 1922.
[2] *Zeitsch. fur Phys.*, **23**, 294 (1924).
[3] *Journ. Phys. Chem.*, **29**, 693 (1925).
[4] *Zeitschr. fur Instrumentenk.*, **26**, 353 (1906).

some transparent medium. Such a screen is exposed to blue light for a quarter to half a minute, which causes the zinc sulphide particles to phosphoresce. It is then immediately exposed to the spectrum for one to two minutes, after which it is at once placed in contact with a photographic plate, sensitive to green light. After two hours the plate is developed in the usual way. The proper ratio of the time necessary for excitation of the screen and exposure must be carefully ascertained by trial. Since the phosphorescence of zinc sulphide is destroyed by infra-red light, it is evident that the presence of a bright line in the spectrum will be denoted by a transparent line in the photographic plate.

The Photography of the Extreme Ultra-Violet.—It has already been stated that the sensitivity of the silver bromide emulsion decreases on the short wave side of the maximum at $\lambda = 4500$ very slowly to about $\lambda = 2400$, after which it decreases very rapidly. This latter decrease is due to the absorptive power of gelatine for all light rays of shorter wave-length than $\lambda = 2400$, and as a result of this no gelatine emulsion is of any use in the photography of the extreme ultra-violet. Silver bromide in the absence of gelatine appears to be sensitive to light of as short wave-length as has as yet been reached.

The limit of the spectrum which can be reached with quartz spectrographs working in air is about $\lambda = 1850$, and consequently there is an unfortunate gap between $\lambda = 2400$ and $\lambda = 1850$, which has a very feeble action on the ordinary photographic plate of commerce. It would be a very great boon to spectroscopists, especially those interested in absorption spectra, were there to be obtained as a standard article of commerce a photographic plate which is sensitive to the usual limit of spectrographic work in air, $\lambda = 2000$.

Two practical methods of solving this difficulty in the laboratory have been successfully used by Duclaux and Jeantet.[1] The first method consists in the removal of the gelatine from the film of an ordinary glass photographic plate by means of sulphuric acid, thereby leaving a film of silver bromide. The plates are placed horizontally in a flat dish containing dilute sulphuric acid prepared by mixing 100 c.c. of the concentrated acid with 1000 c.c. of water. They are allowed to remain for four hours in this solution at a mean temperature of 25°. The plates are then very carefully withdrawn and immersed in water in a second dish, through which a slow stream of water is passed. The washing is complete in thirty minutes, after which the plates are carefully taken out and dried. Since there is only a minute quantity of gelatine left in the film, the plates only take a few minutes to dry.

The film of silver bromide which is left adhering to the glass is quite regular and very sensitive to the rays of short wave-length, but it is very fragile. It is advisable just before developing and fixing to cover the plate with a very thin layer of collodion. This does not

[1] *J. Phys. Radium*, **2**, 154 (1921).

hinder the development if the plate is dipped into water before the collodion film has become dry.

Duclaux and Jeantet did not test the sensitivity of these prepared plates to the extreme ultra-violet by means of a vacuum spectrograph, but it was found that they were very sensitive to as far as $\lambda = 1840$.

The second method is ingenious and depends on the fluorescence of a substance when excited by light of wave-lengths between $\lambda = 2400$ and $\lambda = 1840$. There are many oils which under stimulation by these rays fluoresce with emission of light of longer wave-length than $\lambda = 2400$, which is not absorbed by gelatine. It follows that, if an ordinary plate is covered with a very thin film of such an oil, wherever the extremely short wave light falls on it the fluorescence will produce the latent image at that point. The method works admirably, it being sufficient to cover the plate with the oil film by spreading a few drops of the oil by means of a wad of cotton wool. The most convenient method is to dip the plate in a solution of the oil in alcohol or petrol and allow it to drain and dry. After exposure in the spectrograph it is essential before development to remove the oil film and this may be done by means of a solvent. It is essential for success that this removal of the oil be complete.

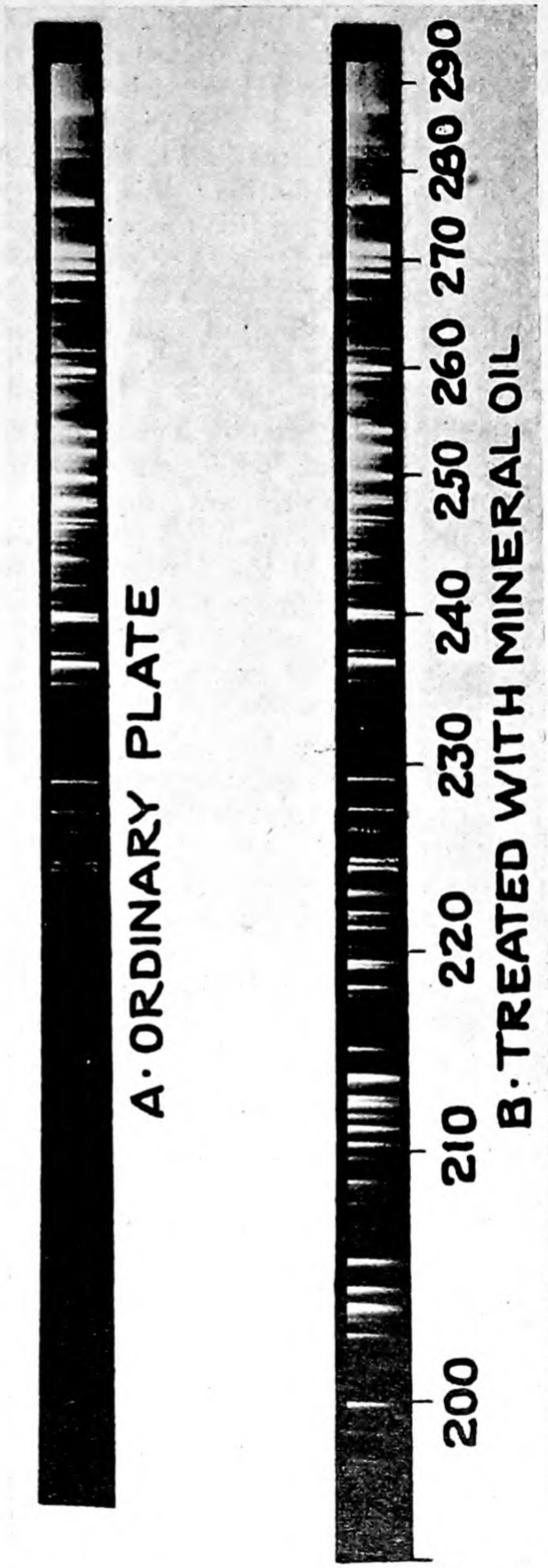


FIG. 95

The results obtained by this method are excellent, great sensitivity being secured. In Fig. 95 are shown two spectrum photographs, one of which has been taken with an oil-treated plate. The improvement at the short wave end is well shown. The only fault that can be found with this method is the tendency to broaden the spectrum lines owing to irradiation; this, however, is less than 0·05 mm.

Lyman [1] has used this process with success in his vacuum spectroscopy down to as far as $\lambda = 580$ A. The process has been critically examined by Harrison.[2] Very satisfactory results are given by the use of a clear paraffin oil such as nujol, which may subsequently be removed by means of acetone.

In his work with the vacuum spectrograph, Schumann used plates coated with silver bromide containing little or no gelatine, the amount of gelatine present, while sufficient to bind the bromide, exerting no appreciable absorption of the light.

Schumann published two papers on the methods of preparation of these plates. In the first paper [3] two alternative processes were described, according to the first of which, pure silver bromide is precipitated from mixed solutions of silver nitrate and potassium bromide (containing excess of the latter), and allowed to settle on plates placed at the bottom of the containing vessel. In the second method the precipitation of the silver bromide is carried out in the presence of a small quantity of gelatine in the solution. Some of the latter is carried down with the silver salt, sufficient to bind the silver salt to the plate, but not to destroy its sensitiveness to the extreme ultra-violet rays. The plates prepared by this method, however, are very slow, and require long exposures.

In his second paper [4] Schumann gave a very much improved method, and one which gives plates that are much more rapid, and at the same time more durable. The outline of the process is as follows: A gelatine emulsion very rich in silver bromide is prepared, and allowed to set to a jelly. It is then washed in cold water and afterwards melted, and mixed with a large volume of water and filtered. The mixture is then poured over the plates which have been laid on a level surface, and allowed to stand. The silver bromide is then deposited on to the plate, and after this the supernatant emulsion is poured off, and the silver bromide film that is left behind is dried. On account of its importance the method may be described in detail.

Two solutions are made as follows:—

A	Potassium bromide . . .	9·0 grms.
	Gelatine (Nelson's No. 1) . .	4·5 ,,
	Distilled water	60 c.c.
B	Silver nitrate	11·25 grms.
	Distilled water	60 c.c.

[1] *Nature*, **112**, 202 (1912).
[2] *J. Opt. Soc.*, America, **11**, 113 (1925).
[3] *Wiener Berichte*, **102**, II., A, 994 (1893).
[4] *Ann. der Physik*, **5**, 349 (1901).

After 20-30 minutes, when the gelatine[1] will be found to be properly swollen and softened, the flasks containing the solutions are both immersed in water at a temperature of 50°-60° C., until the gelatine is completely dissolved. All the following operations must now, of course, be carried out in a brown or red light. The silver solution B is now poured, small portions at a time, into the gelatine solution A (not *vice versa*), the mixture being well shaken after each addition. After the addition of the whole of the solution B, the flask containing the mixture is closed and again thoroughly shaken. The flask is then placed in water at a temperature of 60° C., and allowed to stand quite quietly for half an hour. During this period some of the larger granules of silver bromide settle out. After the half-hour, therefore, the emulsion is poured off very carefully into a porcelain dish, so as not to disturb the precipitate. The dish is placed on ice or in a very cold place (not above 4° C.), and left for 2 to 3 hours, until the emulsion is completely set to a jelly; the firmer the jelly is the better. The jelly is now cut into small pieces with a horn spatula, and these are heaped together on a broad piece of fine muslin, which is then gathered up and tied together to form a bag. This bag is suspended for 2 or 3 hours in running water, or in a 2-litre vessel of water, which is changed ten times at quarter-hour intervals; the water must not be warmer than 14° C. This washing process is carried out to remove the soluble potassium bromide and nitrate. After the washing, the bag is taken out and gently squeezed to remove the adhering water; it is then suspended in a 1½-litre beaker, which contains 950 c.c. freshly boiled water cooled to 55° C. The emulsion melts in a few minutes, and mixes with the water. It is carefully stirred with a glass rod, and twice filtered through glass wool. The glass wool plug should be sufficiently compact to allow the emulsion only to pass slowly. Great care must be taken in the stirring and filtration to guard against the formation of bubbles. The exit tube of the funnel should touch the side of the vessel into which the emulsion runs, so that the stream does not break into drops. The emulsion may now be used at once, or it may once again be allowed to stand, so as to allow the coarser silver bromide to deposit. This makes for a great improvement in the plate, for these coarser particles give dark flecks in the finished picture. For this purpose the emulsion is filtered into a large flat bottomed dish, until the layer is about 4 to 5 mm. deep, when it is allowed to stand for three-quarters of an hour, after which it is carefully poured off, and used at once to coat the plates.

The glass plates require special treatment owing to the thinness of the emulsion, as it is quite impossible to pour a sufficient thickness on to an ordinary plate glass with sharp edges without some of it running off. A piece of emery cloth (not paper) is stretched and pinned down on a flat surface, and the glass plate, held at an angle of

[1] Schumann makes particular note of the fact that Nelson's No. 1 is the only brand of gelatine that is suitable.

30° to the flat surface, is rubbed backwards and forwards on the emery until the sharp angular edge is ground to a rough bevel about ½ mm. wide. Schumann finds that this bevel greatly retards the tendency of the emulsion to run off the plate. The glass plates are then allowed to stand in strong nitric acid for half an hour, then washed with water and dried with a cloth. They are finally polished with a clean cloth, and all dust removed from them, but this should only be done just before the emulsion is poured over them.

When everything is ready for the coating, the plates are all laid on a long narrow piece of plate glass, which stands on feet about 8 to 10 cm. high, and is carefully levelled. Each plate should project 1 to 2 cm. over the edge of the plate glass. In coating large plates it is advisable to measure the emulsion for each plate, *e.g.* 50 to 60 c.c. for a plate 13 × 18 cm., and 25 c.c. for a plate 9 × 13 cm.; for small plates it does not matter. The emulsion is poured very carefully on to the plate, in order to avoid any bubbles being formed. The emulsion is poured on to the projecting edges of the plates, and if it only flows very slowly towards the other end of the plate, the plate may be lifted very gently by putting the finger under the projecting portion. When the whole of the plates are covered, they are left to stand for 3 to 4 hours on the levelling table, in order to allow the silver bromide to settle out. The supernatant emulsion is then poured off, leaving the silver bromide deposit undisturbed, and this is the most delicate part of the process. Schumann's directions here are very precise. The first plate at the left-hand end of the plate-glass table is gently pushed along until it projects about $\frac{4}{10}$ths of its length; an evaporating basin is held underneath, and the plate is slowly lifted with the index finger of the left hand, and turned round the end of the plate-glass table, until the free end of the plate rests on the evaporating basin. The emulsion then runs off, and one can take hold of the plate by the edges at the two upper corners without disturbing the silver bromide deposit. The plate is slowly brought upright and inverted, so that the film side is downwards, and then it is placed on the drying board. This drying board is covered with filter paper, and is provided with a number of vertical wooden pegs, against which the plates are leaned. The plates, when being moved along the levelling table, must only be touched with a knife, the edge of which is pressed against the lower edge of the plate. Touching them with the finger will inevitably cause the emulsion to run on to the levelling table, and not only that particular plate, but the whole batch will be destroyed. In letting the emulsion drain off, great care must be taken not to let the emulsion which runs down the edges find its way over the plate again, or streaks will be produced which materially damage the value of the finished plate.

The drying may be allowed to take place in a dust-free room or preferably in a proper drying chamber, as otherwise zones of varying sensitiveness are liable to be produced. They dry very quickly, usually in about ½ to ¾ hour. If time is a consideration, after the central

portion is dry the still wet ring of emulsion round the edges may be wiped off with a slip of filter paper.

The dried plates may be packed face to face in pairs with very narrow strips of filter paper between them at the edges, in order to prevent the films coming into contact. Each pair should be wrapped separately in black paper. Tinfoil must on no account be used as the plates are very sensitive to it and are quickly fogged. It must be remembered that the film is extremely sensitive to any pressure, so much so that they cannot even be brushed with a soft camel hair brush.

Cutting the plates, therefore, is a very delicate operation, but may be carried out as follows. The plate is laid film up on a table, and a very narrow strip of somewhat thick paper is put along each of the edges of the plate at right angles to the direction in which it is proposed to cut. A straight edge is then rested on these paper strips and the plate cut with a diamond through the film. The paper strips will be found to have damaged the film, and so care must be taken that these strips are so narrow that they will not extend over a part of the film which will be acted on by the light of the spectrum.

The plates prepared according to the above method are not very sensitive during the first few days after their manufacture, and also they do not give very good intensity of image. If, therefore, they are exposed in the spectrograph very soon after being made they must be treated with a very strong developer, one far too strong to be used for the ordinary dry plate without fogging it. On keeping the plates they gain in their sensitiveness and also in the intensity of the image. This is noticeable after 1 to 2 weeks, and after 1 to 2 months they give the best results. After three months a little fog begins to make its appearance. After two years they still give excellent results, but there is then to be noticed a falling off in the intensity.

As a developer Schumann has found nothing to equal Eder's pyrogallol formula, which is as follows :— [1]

A	Sodium sulphite . . .	100 grms.
	Pyrogallol	14 „
	Distilled water	500 c.c.
	Conc. sulphuric acid . . .	6 drops.

The pyrogallol is to be added last of all.

B	Sodium carbonate crystals . .	50 grms.
	Distilled water	50 c.c.
C	Potassium bromide . . .	10 grms.
	Distilled water	100 c.c.

The usual strength of developer for gelatine dry plates is equal parts of A, B, and water, together with 4 to 6 drops of C to every 50 c.c. of the mixture. If the Schumann plates are freshly prepared then equal parts of A and B must be used, and if the intensity is still

[1] Eder's *Handbuch der Photographie*, 1, 225 (W. Knapp, Halle a. S., 1891).

poor a 30 per cent. solution of potassium carbonate may be added drop by drop until, if necessary, as much as one quarter of the volume of the developer has been added. A few drops of C are recommended to keep the plate free from every trace of fog; this also helps to increase the intensity. Schumann also recommends using the developer very cold at the commencement and warming it by rubbing the hand under the dish as soon as the image begins to make its appearance (this is quite feasible since the plates actually exposed by Schumann were very small, *viz.* 13 × 37 mm.). With older plates one should use 1 part of A, 1 part of B, and 1 or 2 parts of water, with 1 to 3 drops of C for every cubic centimetre of A used.

During all processes of development the plate should only be touched with a pair of forceps; it is convenient to leave these attached to the plate throughout the processes of development, fixation, and washing.

As fixing bath a 25 to 30 per cent. solution of sodium thiosulphate (hyposulphite) is used and the unchanged silver bromide dissolves in a few seconds. To wash the plates they should be held for about two minutes under a gentle stream of water, then after this a careful rinsing with distilled water is advisable. The plates are finally set aside in a dust-free place to dry, which in a warm atmosphere takes about 10 to 15 minutes. It must be remembered that the negative is very delicate, and may even be scratched when dusted with a soft brush unless the brush has been very carefully selected.

Generally speaking, these plates are less sensitive than the ordinary dry plate to the rays of longer wave-length than $\lambda = 2200$. They are less acted on, therefore, by the diffused light in the spectrograph.

Plates prepared by a modification of Schumann's method are now prepared by Messrs. Adam Hilger, Ltd., and can be obtained from them. These plates keep remarkably well and are very sensitive to the extreme ultra-violet.

AUTHOR INDEX.

A

Abney, photography of the infra-red, 373.
Adams, E. Q., kryptocyanin, 363.
Adams, W. S., classification of the iron lines, 104.
— — — spectra of sun spots, 61.
Ainslie, spectra of isotopes, 232.
— structure of lithium lines, 231.
Anderson, charging of condensers, 115.
— construction of condensers, 114.
— explosion of wires, 76, 87.
— interferometric measurement of Capella, 48.
— vacuum spark spectrum of calcium, 126.
Ångström, breadth of spectrum lines, 190.
Aronberg, structure of bismuth lines, 181, 189.
Arons, mercury lamp, 97.

B

Babcock, pole effect, 108, 110.
von Baeyer, crossed interferometer plates, 53.
— — structure of bismuth lines, 181, 189.
Baldet, comet tail spectrum, 222, 228.
Baly, effect of pressure in vacuum tubes, 178.
— electrodes for use with the rare gases in vacuum tubes, 162, 165.
— fluorescence and absorption of phenolic ethers, 333.
— occlusion of gases in electrode splash, 171.
— separation of gases in vacuum tubes, 168, 212.
Barbier, dyes for sensitising photographic plates, 363.
Barnard, ultra-microscope, 367.
Barnes, interferometer, 53.
— mercury lamp, 98.
Barratt, secondary spectrum of hydrogen, 166, 203, 208.
— separation of gases in vacuum tubes, 168.
Basquin, bands in flame spectra, 60.
Baxendall, G-band in the solar spectrum, 222.
Becker, explosion of wires, 88.
Becquerel, E., apparatus for spark spectra of solutions, 119.
— — phosphorescence, 236.
— — — and absorption, constant frequency differences in, 261.
— — — decay of, 300, 309.
— — — effect of temperature, 302.
— — — of uranyl salts, 257.
— — — storage of energy, 303.
— — phosphoroscope, 290.
Becquerel, H., constant frequency differences in absorption and fluorescence bands of uranyl salts, 261.
— — resolution of absorption and fluorescence bands at low temperatures, 257, 317.
Benoit, determination of standard metre in terms of the cadmium red line, 1, 10.
Bernard, spectrum of comet, 221.
Berthelot, photochemical change, 255.
Bohr, penetration of electron orbits, 233.
Bolton, fluorescence of uranyl salts, 257.
Borrisow, photophosphorescence of organic compounds, 319.
Bourget, Orion nebula, 44.
Bowen, spectra of ionised carbon, 221.
— — — — oxygen, 213.
Brewster, fluorescence of chlorophyll, 236.
Briggs, photographic plates sensitised by neocyanin, 364.
British Hanovia Quartz Lamp Co., mercury lamps, 100.
Brode, dissolution in water of blue sodium chloride, 308
Brooksbank, spectrum of ionised oxygen, 213.
Bruninghaus, conditions for phosphorescence, 307, 315.
— self-activation in phosphorescence, 311.
Buisson, measurement of wave-length standards, 36.
— origin of secondary spectrum of hydrogen, 204, 208.
— Orion nebula, 44.

Bunsen, impregnated carbon electrodes, 118.
Burns, standard wave-lengths of the lines of iron, 42.
Butler, G-band of the solar spectrum, 222.

C

Cale, fluorescence, 256.
— spectra of isotopes, 232.
Carroll, sensitisation of photographic plates, 377.
Carter, cathodoluminescence spectra, 174.
— vacuum spark spectra, 124.
Chrétien, comet tail spectrum, 221.
Clarke, neocyanin, 364.
Clayton, sensitisation of photographic plates, 357.
Collie, effect of pressure on the spectra of mixed gases in vacuum tubes, 167.
Crew, arc spectra, 94.
Crookes, effect of temperature on phosphorescence, 329.
— phosphorescence of minerals, 237.
— — — rare earths, 315.
— vacuum tubes for study of phosphorescence, 312.

D

Davies, sensitisation of photographic plates by dicyanin, 372.
Davy, arc discharge under liquids, 128.
Delachanal, apparatus for spark spectra of solutions, 119.
Deslandres, band spectra of nitrogen, 214.
— spectra of comets, 221, 230.
Dewar, absorption of gases by charcoal, 171.
— arc spectra, 94.
— — — under water, 128.
— flame spectra, 58.
— self-reversal of spectrum lines, 197.
Dickson, fluorescence of organic compounds, 251.
— resolution of fluorescence bands, 254, 286.
Draper, reversal of photographic plate, 376.
Drummond, phosphorescence of quartz, 102.
Duclaux, photographic plates for extreme ultra-violet, 378.
Duffieux, origin of the secondary spectrum of hydrogen, 208.
Dufour, Zeeman effect in the secondary spectrum of hydrogen, 209.
Dunden, sensitisation of photographic plates by neocyanin, 364.
Dunoyer, optical resonance of sodium vapour, 238.

E

Eagle, band spectra of strontium and barium hydrides, 61.
Eder, flame spectra, 57.
— photographic developer, 383.
— sensitisation of photographic plates by dyes, 358.
Ehrenfest, spectra of isotopes, 232.
Errera, colloid supports for spark spectra, 121.
Exner, variation in intensity in the components of spectrum lines, 190.

F

Fabry, determination of standard wavelengths, 2, 36.
— étalons, 27.
— interferometer, 11.
— origin of secondary spectrum of hydrogen, 204, 208.
— Orion nebula, 44.
— structure of lines, 180.
— trembleur, 94.
Finger, spark spectra under water, 130.
Foote, excitation of nitrogen spectra by electrons, 215.
Fowler, band spectra of carbon monoxide, 221.
— — — — magnesium hydride, 86.
— — — — titanium oxide, 61.
— spectra of ionised carbon, 220.
— — — — nitrogen, 215.
— — — — oxygen, 213.
— vacuum arc, 95.
Frankland, breadth of spectrum lines, 190.
— length of spectrum lines, 196.
Frey, electrodeless ring discharge, 175.
Fulcher, bands in the secondary spectrum of hydrogen, 210.
— excitation of nitrogen spectra by electrons, 215.

G

Gale, classification of the iron lines, 104.
— pole effect, 110.
— structure of spectrum lines, 181.
Galitzin, structure of spectrum lines, 181.
Gaudechon, photochemical change, 256.
Gehrcke, crossed interferometer plates, 53.
— structure of bismuth lines, 181, 189.

Gieseler, absorption spectrum of chromium vapour, 78.
— — — — iron vapour, 76.
Gmelin, structure of spectrum lines, 181.
Goldstein, band spectra of nitrogen, 214.
— blue sodium chloride, 308.
— cathodophosphorescence of organic compounds, 320, 321, 340.
— effect of temperature on phosphorescence, 329.
— spark spectra of salts, 123.
Gottling, fluorescence time interval, 311.
Gouy, flame spectra, 57.
de Gramont, oxyacetylene flame spectra, 59.
— — spark spectra of minerals, 119.
— — — — — solutions, 121.
— — ultimate lines, 123, 147, 196.
Grotrian, absorption spectrum of chromium vapour, 78.
— — — — iron vapour, 76.
Gruhl, phosphorescence of zinc silicate, 307.
Gudden, contradiction of Stokes' rule, 342.
Guntz, phosphorescence of zinc sulphide. 306, 331.
Guye, ultra-microscope, 367.

H

Hackett, resonance spectrum of sodium vapour, 239.
Hagenbach, electrodeless ring discharge, 175.
Hale, spark discharge under liquids, 129.
Halle, kryptocyanin, 363.
Hamy, cadmium lamp, 97.
Hardtke, spectrum of neutral nitrogen atom, 216.
Harrison, sensitisation of plates to extreme ultra-violet, 380.
Hartley, absorption spectrum of benzene, 286.
— band spectra of flames, 60.
— flame spectra, 58.
— fluorescence of mercury vapour, 247.
— persistence of lines, 138, 196.
— quantitative analysis by spark spectra, 134, 147, 151.
— spark spectra, 120.
Haschek, variation in intensity in the components of spectrum lines, 190.
Hemsalech, arc spectra, 94.
— flame spectra, 59, 61.
— mechanism of the spark, 153, 156.
— self-induction in spark circuit, 118.
Henri, absorption spectrum of benzene, 286.
— electric spark under water, 131.
Henri, structure of absorption bands, 289.
Herschel, reversal of photographic plates, 376.
Hertz, cathodoluminescence spectra of metals, 174.
Heurlinger, structure of band spectra, 330.
Hewittic Electric Co., mercury lamps, 100.
Higgs, photography in the red, 359.
Hilger, apparatus for spark spectra, 117.
— Fabry and Perot interferometer, 35.
— pure carbon electrodes, 119.
— wedge spectrograph, 360.
Holladay, sensitivity of normal photographic emulsion, 356.
Homolka, pinacyanol, 362.
Houllevigue, cathododeposition of metals, 35.
Howes, cathodoluminescence of calcite, 309.
— fluorescence of uranyl salts, 257.
— — — — — rate of decay, 260.
— phosphorescence of samaria, 318.
— resolution of flame luminescence bands of lime, 327.
— — — fluorescence bands, 247.
Humphreys, pressure shift of spectrum lines, 104, 129.

I

Imhof, triboluminescence, 306.
Ives, rate of decay of phosphorescence, 309.
— — — — — — effect of temperature, 311.

J

Jackson, phosphorescence of lime, 237.
Janicki, spectra of isotopes, 232.
— structure of spectrum lines, 181.
Jeantet, photographic plates for extreme ultra-violet, 378.
Jewell, multiple self-reversal of spectrum lines, 197.
Johnson, spectra of carbon, 216, 222.
Jones, impregnated electrodes for spark spectra, 119.
Jungjohann, vacuum tubes with Wehnelt cathode, 173.

K

Kayser, error in coincidence method with gratings, 2.
— Kirchhoff's law, 78.

Kayser, self-reversal of spectrum lines, 197.
— spectra of compounds, 177.
— Swan spectrum, 219.
Kearney, fluorescence, 256.
Kent, failure of condensed spark as source of standard wave-length, 71.
King, band spectra of compounds, 61.
— cathodoluminescence spectra, 174.
— electric resistance furnace spectra, 62, 107, 110.
Klatt, excitation of phosphorescence, 290.
— phosphorescence of alkaline earth sulphide preparations, 293.
— self-activation of fluorite, 311.
Konen, arc discharge under liquids, 128.
— spark discharge under liquids, 129.
— Swan spectrum, 220.
— vacuum tubes with Wehnelt cathode, 173.
König, isocyanin dyes, 362.
Kossel, spectroscopic displacement law, 133.
von Kowalski, photophosphorescence of organic compounds, 319, 340.
Kratzer, structure of band spectra, 330.
Krulla, apparatus for spark spectra, 121.

L

de Làszlò, electric spark under water, 131.
Lehmann, phosphoro-photographic process, 377.
— photographic plates sensitised by alizarin blue, 361.
Leimbach, sensitivity of normal photographic emulsions, 356.
Lembert, spectra of isotopes, 230.
Lemon, structure of spectrum lines, 181.
Lenard, excitation of phosphorescence, 290.
— phosphorescence of alkaline earth sulphide preparations, 293.
— self-activation of fluorite, 311.
Lenz, structure of band spectra, 330.
Leonard, persistence of spectrum lines and quantitative analysis, 134, 138.
Levy, fluorescence of barium platinocyanide, 306.
Lewis, cathodoluminescence spectra, 174.
van der Lingen, fluorescence of mercury vapour, 248.
Liveing, arc spectra, 94.
— — — under water, 128.
— flame spectra, 58.
— self-reversal of spectrum lines, 197.
Lockyer, arc spectra, 58.
— enhanced lines, 132.
— length of spectrum lines, 196.
— self-reversal of spectrum lines, 197.
Lockyer, spark spectra under water, 129.
Loving, vacuum arc, 95.
— — sparks, 124.
Luckiesh, rate of decay of phosphorescence, 309.
— — — — — — effect of temperature, 311.
Lumière, dyes for sensitising photographic plates, 363.
Lummer, interferometer plate, 53.
Lunelund, structure of spectrum lines, 181.
Lunt, spectra of doubly ionised oxygen, 213.
Luppo-Cramer, reversal of photographic plates, 377.
Lyman, photography of extreme ultra-violet, 380.

M

McDowell, fluorescence of uranyl salts, 257.
— phosphorescence of uranyl salts, 260.
McLennan, fluorescence, 256.
— photography of infra-red, 363, 365.
— spectra of isotopes, 232.
— structure of lithium lines, 231.
McVicker, fluorescence of benzene vapour, 254.
— Tesla luminescence spectra, 283, 285, 287.
Marsh, fluorescence of benzene vapour, 254.
— Tesla luminescence spectra, 283, 285, 287.
Masson, arc spectra under liquids, 128.
Mees, sensitisation of photographic plates to yellow, red, and infra-red, 357, 367.
Meggers, correction for change of phase at reflection, 42.
— photography of the infra-red, 363.
— standard wave-lengths of iron lines, 42.
Meissner, relative intensities of satellites of spectrum lines, 232.
Mermet, apparatus for spark spectra, 119.
Merrill, interferometric measurement of Capella, 50.
— sensitisation of photographic plates by dicyanin, 372.
— standard wave-lengths of iron lines, 42.
Merritt, fluorescence of uranyl salts, 257.
Merton, classification of lines of secondary spectrum of hydrogen, 209, 211.
— introduction of hydrogen into vacuum tubes, 166.

Merton, origin of secondary spectrum of hydrogen, 203.
— separation of gases in vacuum tubes, 168, 212.
— spectra of carbon, 222.
— — — isotopes, 230.
— — — nitrogen, 216.
Michelson, breadth of spectrum lines, 191.
— determination of standard metre in terms of wave-lengths of cadmium lines, 10.
— interferometer, 1.
— — application to astronomy, 47.
— interferometric measurement of diameter of Betelgeux, 50.
— structure of spectrum lines, 9, 179.
— visibility of interference fringes, 4.
Miethe, sensitisation of photographic plates by ethyl red, 362.
Millikan, spectra of ionised carbon, 221.
— — — — oxygen, 213.
— vacuum sparks, 124.
Millochau, reversal of photographic plates, 376.
Milner, mechanism of the electric spark, 156.
Mitscherlich, flame spectra, 56.
Mohler, excitation of nitrogen spectra by electrons, 215.
— mechanism of the electric spark, 157.
— spark spectra under liquids, 129.
Moore, optical resonance of sodium vapour, 239.
Morton, fluorescence of uranyl salts, 257.

N

Nagaoka, pole and Zeeman effects, 112.
— spectra of isotopes, 232.
— structure of spectrum lines, 181, 188.
— vacuum arc, 95.
Newall, G-band of the solar spectrum, 222.
Nichols, cathodoluminescence of oxides, 328.
— flame luminescence, 322.
— fluorescence of uranyl salts, 253, 257.
— phosphorescence of calcite, 309.
— — — calcium sulphide phosphore, 327.
— — — uranyl salts, 260, 316.
— phosphoroscope, 292.
Nutting, spectra of mixed gases, 168.

O

Olmsted, band spectrum of calcium hydride, 61, 86.
Onnes, resolution of absorption and fluorescence bands at low temperatures, 257, 262, 317.

P

Paschen, spectrum of oxygen, 213.
Paton, vacuum sparks, 126.
Payn, vacuum arc, 95.
Pease, interferometric measurement of diameter of Betelgeux, 50.
Perot, determination of standard wave-lengths, 2.
— étalons, 27.
— interferometer, 11.
— trembleur, 94.
— structure of spectrum lines, 180.
Perrin, theory of fluorescence, 255.
Pfund, arc, 92.
— mercury lamp, 98.
Pilley, spectra of nitrogen, 216.
Plücker, band spectra of nitrogen, 214.
— design of vacuum tubes, 159.
— spectrum of oxygen, 213.
Pluvinel, comet tail spectrum, 222.
Pollok, persistence of spectrum lines and quantitative analysis, 134.
Pringsheim, fluorescence of benzene vapour, 288.

R

Ramage, banded spectra of flames, 60.
Ramsay, effect of pressure on spectra of mixed gases in vacuum tubes, 167.
Rayet, stellar spectra, 199.
Rayleigh, breadth of spectrum lines, 191, 195, 204.
— relation between temperature and visibility of interference fringes, 204.
Reimann, fluorescence of benzene vapour, 288.
Reis, spectra of flames, 59.
Rice, absorption and fluorescence of phenolic ethers, 333.
Richards, spectra of isotopes, 230.
Riding, occlusion of gases in electrode splash, 171.
Ritz, photography of the infra-red, 375.
Roberts-Austen, oxy-hydrogen flame spectra, 58.
Rossiger, fluorescence and concentration, 252.
Rowland, vacuum sparks, 124.
Royds, mechanism of the electric spark, 156.
Runge, spectrum of oxygen, 213.

S

Saha, relation between absorption and emission by metallic vapours, 81, 85.
— depression of ionisation of the atoms of a metal in the presence of a second metal, 83.
St. John, classification of iron lines, 107.
— — pole effect, 108, 110.
Sawyer, explosion of wires, 88.
— vacuum sparks, 124, 126.
Schenck, mechanism of the electric spark, 154.
Schleede, phosphorescence of zinc silicate, 307.
Schmidt, influence of temperature on phosphorescence, 329.
— discharge of phosphorescence by infra-red rays, 354.
Schmieder, quantitative relation between absorption and phosphorescence, 338.
Schoen, sensitisation of photographic plates by neocyanin, 364.
Schonrock, relation between temperature and visibility of interference fringes, 204.
Schumacher, electrodeless ring discharge, 175.
Schumann, photography of the extreme ultra-violet, 380.
Schuster, mechanism of electric spark, 153.
— self-induction in spark spectra, 118.
— spectra of oxygen, 213.
Smithells, Swan spectrum, 220.
Soddy, absorption of gases by calcium, 170.
Sommerfeld, law of spectroscopic displacement, 133.
Stansfield, structure of spectrum lines, 181.
Stark, self-activation in fluorescence, 311.
— ultra-violet fluorescence, 250, 286.
Steubing, fluorescence of mercury vapour, 249.
Stewart, Tesla luminescence, 283, 287, 344.
Stokes, fluorescence of uranium compounds, 256.
— law of fluorescence and absorption, 236, 251, 288, 304, 338, 342.
Stratton, astronomical physics, 133.
Strutt, R. J., optical resonance of sodium vapours, 238.
Sugiura, structure of spectrum lines, 181, 188.
— vacuum arc, 95.

T

Tailfer, sensitisation of photographic plates by eosin, 357.
Takamine, structure of spectrum lines, 181, 187, 188, 189.
Tatnall, apparatus for arc spectra, 94.
Taylor, sensitivity of normal photographic emulsions, 356.
Terenin, reversal of photographic plate, 377.
Traube, sensitisation of photographic plates by ethyl red, 362.
Travers, manipulation of gases, 162.
Tutton, crystalline structure and chemical constitution, 268.
Twyman, wave-length tables for spectrum analysis, 149.

U

Urbain, conditions for phosphorescence, 307, 315.
— phosphorescence of rare earths, 237.
— vacuum tubes for phosphorescence, 313.

V

Valenta, flame spectra, 57.
Valentiner, fluorescence and concentration, 252.
Vogel, sensitisation of photographic plates by dyes, 357.

W

Wali-Mohammad, structure of spectrum lines, 181.
Walmsley, structure of spectrum lines, 181.
Walters, sensitisation of photographic plates by dicyanin, 372.
Ware, classification of the spectrum lines of iron, 107.
Waterhouse, reversal of photographic plate, 376.
— sensitisation of collodion emulsion by eosin, 357.
de Watteville, arc spectra, 94.
— — flame spectra, 57, 59, 61.
Watts, Swan spectrum, 220.
Wehnelt, Wehnelt cathode, 172.
Whelan, persistence of spectrum lines, 134.
Whitney, pole effect, 110.
Wick, fluorescence of uranyl salts, 257.
— phosphorescence of uranyl salts, 260.

Wiedemann, discharge of phosphorescence by infra-red rays, 354.
— influence of temperature on phosphorescence, 329.
— phosphoroscope, 291.
— Wehnelt cathode, 172.
Wilber, cathodoluminescence of oxides, 328.
— flame luminescence, 322.
— fluorescence of uranyl salts, 257.
— rate of decay of phosphorescence, 309.
Wilkinson, Swan spectrum, 220.
Wilsing, spark discharge under liquids, 129.
Wolf, stellar spectra, 199.
Wood, action of light on fluorescent compounds, 255.
Wood, fluorescence of mercury vapour, 247.
— magnetic rotation spectrum of sodium vapour, 242.
— resonance spectrum of mercury vapour, 238.
— — — — sodium vapour, 238.
— self-reversal of red hydrogen lines, 197.
— spectrum of atomic hydrogen, 200.
— transparency of *p*-nitrosodimethylaniline to ultra-violet light, 298.
— vacuum sparks, 124.
Wright, photography by means of infra-red light, 365.
Wüllner, breadth of spectrum lines, 190.
— spectrum of oxygen, 213.

SUBJECT INDEX.

A

Absorption and emission by metallic vapours, relation between, 79, 85.
— — — in fluorescence and phosphorescence, Stokes' law, 236, 251, 288, 304, 338, 342.
— — fluorescence, reversal region, 262, 275.
— — radiation of energy in fluorescence and phosphorescence, 235.
— bands and reactivity, 335.
— — constant frequency differences in, 254, 257, 261, 286, 343.
— — of benzene, 286.
— — — piperidine, 336.
— — — pyridine, 336.
— — — trinitrobenzene, 336.
— — — uranyl salts, 261.
— — — — — — polarisation of, 278.
— — — — — — resolution at low temperatures, 274.
— — relation with energy content, 336.
— — source of light for, 131.
— of light, Beer's law, 350.
— lines of metallic vapours, 76.
Acridine orange for sensitising photographic plates, 362, 370.
Alizarine blue for sensitising photographic plates, 359.
Alkaline metal halides, effect of X-rays and cathode rays on, 308.
— — — spark spectra of, 123.
Aluminium lines, persistence of, 141.
— — sensitive and ultimate, 150.
— oxide, flame luminescence of, 325.
— — phosphorescence of, 237.
Ångström bands of carbon, 219.
Antarian bands, 86.
Antimony lines, persistence of, 144.
— — sensitive and ultimate, 150.
Arc, Pfund, 92, 111.
— rotated, 91, 94.
— spectra, 90.
— under liquids, 128.
— vacuum, 95.
— with cored carbons, 94.
Arsenic lines, persistence of, 144.
— — sensitive and ultimate, 150.
Autunite, fluorescence of, 256.

B

Band spectra, 177.
— — given in electric furnace, 85.
— — of carbon oxides, 219.
— — — nitrogen, 214.
— spectrum of calcium hydride, 85.
— — — magnesium hydride, 85.
— — — oxygen, 213.
— — — titanium oxide, 85.
Bands in flame spectra, 59, 60.
Barium lines, persistence of, 140.
— — sensitive and ultimate, 150.
— platinocyanide, fluorescence of, 306.
Beer's law, 350.
Benzene, absorption bands of, 286.
— fluorescence of, 287.
— photophosphorescence of, 321.
— Tesla luminescence spectrum of, 285.
Beryllium lines, sensitive and ultimate, 150.
— oxide, phosphorescence of, 237.
Betelgeux, interferometric measurement of the diameter of, 50.
Bismuth lines, persistence of, 144.
— — sensitive and ultimate, 150.
— — structure of, 188.
Bohr theory, 82, 132, 220, 233, 330.
Boric acid, flame luminescence of, 325.
Boron lines, sensitive and ultimate, 150.
Breadth of spectrum lines, 190.

C

Cadmium lamp, 97.
— lines, breadth of, 192.
— — persistence of, 140.
— — sensitive and ultimate, 150.
— — structure of, 10, 180, 188.
— phosphate, flame luminescence of, 325.

Cæsium lines, persistence of, 139.
— — sensitive and ultimate, 150.
Calcite, flame luminescence of, 325.
— rate of decay of phosphorescence, 309.
Calcium, H and K lines of, 68.
— hydride, band spectrum of, 85.
— lines, persistence of, 140.
— — sensitive and ultimate, 150.
— sulphide, flame luminescence of, 325.
— — phosphores, 295.
— use of in exhausting apparatus, 170.
Capella, interferometric measurement of, 48.
Carbon, arc spectrum of, 228.
— dioxide, Ångström bands of, 219.
— — Merton bands of, 225.
— lines, enhanced, 220.
— — sensitive and ultimate, 150.
— monoxide, comet tail spectrum, 221.
— — Fowler high-pressure bands of, 221.
— — Swan spectrum, 219.
Cathode, Wehnelt, 172.
Cathodoluminescence of oxides, 328.
— — — temperature limits of, 329.
— spectra of metals, 174.
Cathodophosphorescence, 260, 312, 318.
— of organic compounds, 321.
— — xylene, 322.
Celtium lines, sensitive and ultimate, 150.
Cerium lines, persistence of, 143.
— — sensitive and ultimate, 150.
Chalcocite, fluorescence of, 256.
Change of phase at reflection, 29, 39, 42.
Charcoal, use of in exhausting apparatus, 171.
Chlorophyll, fluorescence of, 236.
Chromium lines, absorption, 78.
— — low temperature, 78.
— — persistence of, 144.
— — sensitive and ultimate, 150.
Cobalt lines, persistence of, 147.
— — sensitive and ultimate, 150.
Coerulin for sensitising photographic plates, 359.
Comet 1910*a*, 222.
— Borelly, 221.
— Morehouse, 221.
— tail spectrum, 221.
Condenser, charging of, 115.
— construction of, 87, 88, 114, 124.
Constant frequency differences in absorption bands, 261, 343.
— — — — fluorescence bands, 261, 343.
— wave-length differences in magnetic rotation spectra, 244.
— — — — resonance spectra, 239.
Continuous spectra, 177.
Copper lines, persistence of, 139.
— — sensitive and ultimate, 150.
Cored carbons for arc spectra, 94.
Corundum, flame luminescence of, 325.

D

Diamond, phosphorescence of, 237.
Dicyanin, for sensitising photographic plates, 362, 371.
Discharge, arc, 90, 95.
— — under liquids, 128.
— electrodeless ring, 175.
— spark, 112, 124.
— — under liquids, 128.
Dissociation of hydrogen in vacuum tubes, 200.
Doppler effect, 191, 204.

E

Electrical resistance furnace spectra, 62.
— — — band spectra, 85.
Electrodeless ring discharge, 175.
Electrodes for vacuum tubes, 159.
— impregnated for spark spectra, 118, 121.
Emerald, phosphorescence of, 237.
Emission and absorption by metallic vapours, relation between, 79, 85.
Energy quantum theory, 337.
Enhanced lines, 69, 132.
— — influence of other vapours on, 83.
Erbium lines, sensitive and ultimate, 150.
Erythrosin, for sensitising photographic plates, 362, 373.
Étalon, 27.
Ethyl red for sensitising photographic plates, 362.
Europium lines, sensitive and ultimate, 150.
Exhaustion by means of charcoal, 171.
— — — — metallic calcium, 170.
Explosion of wires, 86.

F

Fabry and Perot interferometer, 17.
— — — — application of, to the Orion nebula, 44.
Flame luminescence, constant frequency differences in, 327.
— — excitation of, 323.
— — temperature limits of, 323, 325.
— spectra, 56.
Fluorescence, 234.
— a theory of, 329.
— activated state of molecules, 334.
— and absorption, reversal region, 262, 275.

Fluorescence and phosphorescence, differentiation between, 339.
— — — Stokes' law, 236, 251, 304, 338, 342.
— bands, constant frequency differences in, 261, 343.
— — resolution of, at low temperatures, 253, 257, 268.
— — structure of, 261.
— effect of concentration on, 252.
— of barium platinocyanide, 306.
— — benzene, 287.
— — chlorophyll, 236.
— — gases and solutions, 246.
— — mercury vapour, 247.
— — organic compounds, 250.
— — uranyl salts, 256.
— — — — effect of crystalline form, 282.
— — — — polarisation of, 277.
— — — — resolution at low temperatures, 268.
— Perrin's theory of, 255.
— persistence of, 258, 341.
— rate of decay, 258, 310, 342.
— relation with absorption of light, 333.
— reversal of, 262, 275.
— time interval, 311.
Fluorite, flame luminescence of, 325.
— phosphorescence of, 303, 311.
— self-activation of, 311.
Fulcher bands in secondary spectrum of hydrogen, 209.

G

Gallium lines, sensitive and ultimate, 150.
Gases, separation of in vacuum tubes, 212.
— spectra of, 157.
— — — effect of pressure on, 167.
Germanium lines, sensitive and ultimate, 150.
Glucinum lines, sensitive and ultimate, 150.
— — phosphorescence of, 237.
Gold lines, wave-lengths of, 137.
— — persistence of, 139.
— — sensitive and ultimate, 150.

H

H and K lines of calcium, 68.
Half-width of spectrum lines, 7, 191.
Hydrocarbon band spectrum, 222.
Hydrogen, classification of lines in the secondary spectrum, 209.
— dissociation of, in vacuum tubes, 200.
— lines, breadth of, 192.
Hydrogen lines, structure of, 9, 179.
— molecule, spectrum of, 200.

I

Indium lines, persistence of, 141.
— — sensitive and ultimate, 150.
Induction coil, 112.
Intensity of spectrum lines, 127.
Interference fringes, limit of visibility of, 204, 208.
— — visibility of, 4.
— point patterns, 182.
Interferometer, Barnes, 53.
— Fabry and Perot, 17, 27.
— methods, Fabry and Buisson, 36.
— — Fabry and Perot, 11.
— — Michelson, 1.
— Michelson, 2.
— plate, Lummer and Gehrcke, 53.
Interferometers, crossing of, 181.
Interferometric measurement of Orion nebula, 44.
— — — stellar magnitudes, 47, 50.
Iridium lines, sensitive and ultimate, 150.
Iron lines, absorption, 77.
— — low temperature, 77, 106.
— — Mount Wilson classification of, 103.
— — persistence of, 146.
— — pole effect of, 108.
— — sensitive and ultimate, 150.
— — temperature classification of, 74.
Isotopes, spectra of, 230.

K

Kryptocyanin for sensitising photographic plates, 363, 371.
Kunzite, flame luminescence of, 325.

L

Lamp, cadmium, 97.
— mercury vapour, 97.
— — — deterioration of, 101.
Lanthanum lines, persistence of, 141.
— — sensitive and ultimate, 150.
Law, Beer's, 350.
— of spectroscopic displacement, 133.
— Stokes', 236, 251, 288, 304, 338, 342.
Lead isotopes, spectra of, 230.
— lines, persistence of, 142.
— — sensitive and ultimate, 150.
Length of spectrum lines, 196.
Lepidolite, phosphorescence of, 237.

Lime, flame luminescence of, 325, 327.
— phosphorescence of, 237.
Lithium isotopes, spectra of, 231.
— lines, persistence of, 139.
— — sensitive and ultimate, 150.
Low temperature lines of chromium, 78.
— — — — iron, 77.
— — — — manganese, 78.
Luminescence, 234.
— flame excitation of, 322.
— spectra, Tesla, 283.
Lutecium lines, sensitive and ultimate, 150.

M

Magnesium hydride, band spectrum of. 85.
— lines, persistence of, 140.
— — sensitive and ultimate, 150.
— oxide, flame luminescence of, 325.
Magnetic rotation spectrum of sodium vapour, 242.
Manganese lines, absorption, 78.
— — low temperature, 78.
— — persistence of, 146.
— — sensitive and ultimate, 150.
Many line spectrum of hydrogen, 200.
Mars, photography of, 365.
Mechanism of the spark, 153.
Mercury lines, breadth of, 192.
— — persistence of, 140.
— — sensitive and ultimate, 150.
— — structure of, 180, 182.
— pump, diffusion, 169.
— — Gaede, 169.
— — molecular, 169.
— — Sprengel, 168.
— — Toepler, 168.
— vapour, active state of, 248.
— — fluorescence of, 247.
— — lamp, 97.
— — — deterioration of, 101.
— — resonance spectrum of, 238.
Metallic vapours, absorption and emission by, 79, 85.
— — — vapour of, 76.
Michelson interferometer, 2.
— — application of, to measurements of stellar magnitudes, 47, 50.
Minerals, phosphorescence of, 237.
Molecules, activated state of, 331, 332, 334.
— band spectra of, 199.
— different energy states of, 335.
— reactivity and absorption spectra of, 334.
Molybdenum lines, persistence of, 145.
— — sensitive and ultimate, 150.

N

Naphthacyanol for sensitising photographic plates, 362, 370.
Neocyanin for sensitising photographic plates, 364, 372.
Neodymium lines, sensitive and ultimate, 150.
Nickel lines. persistence of, 147.
— — sensitive and ultimate, 150.
Niobium lines, sensitive and ultimate, 150.
Nitrogen, spectra of, 214.
Non-metals, spark spectra of, 123.
Novæ, 199.

O

Optical resonance, 237.
— — of mercury vapour, 238.
— — — sodium vapour, 238.
Order of interference, 39, 46.
Organic compounds, cathodophosphorescence of, 321.
— — fluorescence of, 322.
— — photophosphorescence of, 319.
Orion nebula, interferometric measurements of, 44.
Orthochrome T for sensitising photographic plates, 362, 370.
Oxy-acetylene flame spectra, 59.
Oxy-hydrogen flame spectra, 58.
Oxygen lines, breadth of, 192.
— — structure of, 179.
— spectra of, 213.

P

Palladium lines, sensitive and ultimate, 150.
Persistence of fluorescence, 341.
— — phosphorescence, 234.
— — — effect of temperature, 302
— — — relation with intensity, 299, 331.
— — spark lines, 135, 148.
Pfund arc, 111.
Phenolic ethers, absorption spectra and fluorescence of, 333.
Phosphores, effect of pressure on, 294, 306.
— flame luminescence of, 325, 328.
— preparation of, 294.
Phosphorescence, 234, 289.
— a theory of, 329.
— activated state of molecules, 331.
— and absorption of energy, 338.
— and fluorescence, differentiation between, 339.

Phosphorescence at low temperatures, 319.
— constant frequency differences in, 343.
— dependence on physical state, 317.
— effect of concentration, 293.
— — — temperature, 301, 302.
— fatigue effect, 347.
— individuality of the bands, 304, 346, 355.
— instantaneous bands, 304, 352.
— metastable states, 308.
— of alkaline earth sulphide preparations, 298.
— — alumina, 237.
— — diamond, 237.
— — emerald, 237.
— — fluorite, 303, 311.
— — glucina, 237.
— — lepidolite, 237.
— — lime, 237.
— — organic compounds, 319.
— — rare earths, 237, 316.
— — samaria, 318.
— — spodumene, 237.
— — uranyl salts, 260.
— optimum of, 316, 320, 348, 351.
— quenching by infra-red rays, 354.
— rate of decay, 300, 308.
— relation between frequencies of activating and radiated energy, 340, 345.
— relation between intensity and persistence, 299, 331.
— resolution of bands in, 317.
— stability of the activated state, 346.
— storage of energy, 308.
— the three temperature conditions, 304.
Phosphorogen, 316.
Phosphoroscope, 237, 290, 310.
Phosphorus lines, sensitive and ultimate, 151.
Photographic plate, bathing technique, 368.
— — region of sensitivity, 356.
— — sensitisation to extreme ultra-violet, 378.
— — — — yellow, red, and infra-red, 357.
— — sensitising solutions, 369.
— — sensitivity, curve of, 357.
Photography by short wave infra-red light, 365.
— of Mars, 365.
— — extreme ultra-violet, 378, 380, 384.
— — the red and infra-red, Abney's method, 373.
— — — — — — — reversal method, 376.
— — — — — — — phosphoro-photographic method, 377.
Photography of the red and infra-red, Ritz's method, 375.
— — — spectrum, 356.
Photophosphorescence of benzene, 321.
— — organic compounds, 319.
— — xylene, 322.
Pinachrome for sensitising photographic plates, 362, 370.
Pinacyanol for sensitising photographic plates, 362, 370.
Pinaflavol for sensitising photographic plates, 363, 370.
Pinaverdol for sensitising photographic plates, 362, 370.
Piperidine, absorption spectra of, 336.
Platinum lines, sensitive and ultimate, 151.
Plurality of spectra, 199.
Polarisation of absorption bands of uranyl salts, 278.
— — fluorescence bands of uranyl salts, 277.
Pole effect, 108.
— — relation with Zeeman effect, 112.
Potassium lines, persistence of, 139.
— — sensitive and ultimate, 151.
Pump, mercury, diffusion, 169.
— — Gaede, 169.
— — Sprengel, 168.
— — Toepler, 168.
— molecular, 169.
— oil, 169.
Pyridine, absorption spectra of, 336.

Q

Quantitative analysis by spark spectra, 134.
Quartz, deterioration of transparency, 101, 308, 332.
Quinaldine red, for sensitising photographic plates, 372.

R

Radium lines, sensitive and ultimate, 151.
Rare earths, phosphorescence of, 237, 316.
Reactivity and absorption spectra, 335.
Reflection, change of phase at, 29.
Resolution of absorption bands at low temperature, 274.
— — fluorescence bands at low temperature, 268.
Resonance radiation, 237.
— spectra, 237.
— spectrum of mercury vapour, 238.
— — — sodium vapour, 238.

Reversal of lines given by spark discharge under liquids, 129.
— — region in fluorescence spectra, 262, 275.
— — spectrum lines, 196.
Rhodamine B for sensitising photographic plates, 372.
Rhodium lines, sensitive and ultimate, 151.
Ring discharge, electrodeless, 175.
Rowland's standard, errors in, 34.
Rubidium lines, persistence of, 139.
— — sensitive and ultimate, 151.
Rubies, synthetic, flame luminescence of, 325.
Ruthenium lines, sensitive and ultimate, 151.

S

Samarium oxide, phosphorescence of, 318.
Sapphires, white, flame luminescence of, 325.
Satellites of spectrum lines, symmetry in, 184.
Scandium lines, sensitive and ultimate, 151.
Secondary spectrum of hydrogen, 200.
— — — — classification of lines, 209.
— — — — origin of, 203.
— standard wave-lengths, determination of, 36.
Self-induction, elimination of air lines by, 118, 153.
Self-reversal of spectrum lines, 197.
Sensitive lines, 148.
Sensitol green for sensitising photographic plates, 363.
— red for sensitising photographic plates, 363.
Separation of gases in vacuum tubes, 212.
Sidot blende, flame luminescence of, 325.
Silica, flame luminescence of, 325.
— fused, deterioration of transparency, 101, 308, 332.
Silicon lines, persistence of, 141.
— — sensitive and ultimate, 151.
Silver lines, persistence of, 139.
— — sensitive and ultimate, 151.
Sodium lines, breadth of, 192.
— — persistence of, 139.
— — sensitive and ultimate, 151.
— — structure of, 179.
— vapour, magnetic rotation spectrum of, 242.
— — resonance spectrum of, 238.
Spark discharge, 112, 124.
— — mechanism of, 153.
— — under liquids, 128.
Spark discharge under water as source of light for absorption spectra, 131.
— spectra, 112.
— — air lines in, 118, 153.
— — of alkali metal halides, 123.
— — — non-metals, 123.
— — — solutions, 119.
— — quantitative analysis by, 134.
— vacuum, 124.
— — fatigue effect in, 125.
Spectra, arc, see under Arc spectra.
— band, 177.
— cathodoluminescence, of metals, 174.
— continuous, 177.
— of carbon, 220, 228.
— — — oxides, 219, 221, 225.
— — compounds, 177.
— — gases, 157.
— — — effect of pressure on, 167.
— — isotopes, 230.
— — nitrogen, 214.
— — oxygen, 213.
— plurality of, 199.
— spark, see under Spark spectra.
Spectrograph, wedge, 358.
Spectroscopic displacement, law of, 133.
Spectrum lines, breadth of, 190.
— — character of, 178.
— — enhanced, 69, 83, 132.
— — half-width of, 7, 191.
— — intensity of, 127.
— — of iron, Mount Wilson classification of, 103.
— — — — pole effect, 103.
— — length of, 196.
— — persistence of, 135, 148.
— — reversal of, 129, 196.
— — satellites of, symmetry in, 184.
— — sensitive, 148.
— — structure of, 179.
— — temperature classification of, 62.
— — ultimate, 148.
— secondary of hydrogen, 200.
Spodumene, phosphorescence of, 237.
Sprengel pump, 168.
Stars, Wolf-Rayet, 199.
Steel, quantitative analysis of, by ultimate lines, 152.
Stokes' law, 236, 251, 288, 304, 338, 342.
Strontium lines, persistence of, 140.
— — sensitive and ultimate, 151.
Structure of spectrum lines, 179.
Swan spectrum, 219.

T

Tantalum lines, sensitive and ultimate, 151.
Telluric acid, flame luminescence of, 325.

Tellurium lines, sensitive and ultimate, 151.
Temperature classification of spectrum lines, 62.
Tesla luminescence spectra, 283, 344.
Thallium isotopes, spectra of, 230.
— lines, breadth of, 192.
— — persistence of, 141.
— — sensitive and ultimate, 151.
— — structure of, 180.
Thermoluminescence, 234.
Thorium lines, persistence of, 143.
— — sensitive and ultimate, 151.
Tin lines, persistence of, 141.
— — sensitive and ultimate, 151.
Titanium lines, persistence of, 142.
— — sensitive and ultimate, 151.
— oxide, band spectrum of, 85.
Toepler pump, 168.
Trembleur, 94.
Triboluminescence, 234, 306.
Trinitrobenzene, absorption spectra of, 336.
Tube arc, 70.
— resistance furnace, 62.
Tungsten lines, persistence of, 145.
— — sensitive and ultimate, 151.

U

Ultimate lines, 148.
Uranium lines, persistence of, 145.
Uranyl salts, absorption bands, 261.
— — effect of crystalline form of fluorescence, 282.
— — fluorescence of, 256.
— — phosphorescence of, 260.
— — polarisation of absorption bands, 278.
— — — — of fluorescence bands, 277.
— — resolution of absorption bands at low temperatures, 274.
— — — — fluorescence bands at low temperature, 268.

V

Vacuum arc, 95.
— spark, 124.
Vacuum spark, fatigue effect in, 125.
— tubes, construction of, 159.
— — filling of, 162.
— — separation of gases in, 212.
Vanadium lines, persistence of, 144.
— — sensitive and ultimate, 151.
Vibrator, 94.
Visibility curves, 5.
— of interference fringes, 4.
— — — — limit of, 46, 204, 208.

W

Wave-length standards, errors in Rowland's, 34.
Wave-lengths, determination of secondary standard, 36.
Wedge spectrograph, 358.
Wehnelt cathode, 172.
Wolf-Rayet stars, 199.

X

Xylene, cathodophosphorescence of, 322.
— fluorescence of, 322.
— photophosphorescence of, 322.

Y

Ytterbium lines, sensitive and ultimate, 151.
Yttrium lines, persistence of, 141.
— — sensitive and ultimate, 151.

Z

Zinc lines, breadth of, 192.
— — persistence of, 140, 141.
— — sensitive and ultimate, 151.
— — structure of, 180.
— oxide, flame luminescence of, 325.
— sulphide, flame luminescence of, 325.
Zirconium lines, persistence of, 142.
— — sensitive and ultimate, 151.
— oxide, flame luminescence of, 325.

PRINTED IN GREAT BRITAIN BY THE UNIVERSITY PRESS, ABERDEEN